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Combustion Additives for Pollution Control - A State-of-the-Art Review

Battelle Columbus Labs, Ohio

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EPA-600/2-77-008a

January 1977

**COMBUSTION ADDITIVES
FOR POLLUTION CONTROL--
A STATE-OF-THE-ART REVIEW**

by

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Prepared for

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ABSTRACT

Fuel additives have been used, or proposed for use, to serve a variety of functions in combustion systems. This report covers a state-of-the-art review of combustion-type fuel additives as to their potential in reducing air-pollutant emissions for oil and coal firing. The report contains two complementary parts: (1) a review of combustion mechanisms as they relate to additive action in controlling emissions, and (2) a review of experimental investigations of combustion-type fuel additives.

The review of technical literature revealed relatively limited quantitative data from experimental investigations on combustion additives in which conditions are well defined. However, there is evidence for some measure of control of emissions by fuel additives.

The evidence for control by fuel additives of visible smoke and carbon particulate is relatively strong, and the evidence for control of polycyclic organic matter (POM) is somewhat weaker. The evidence for control of NO_x is quite weak. Significant control of SO_2 or total sulfur emissions by fuel additives does not appear to be possible, although emissions of SO_3 can be reduced. Possibilities for the control of emissions of ash, or specific ash constituents by fuel additives, is restricted to enhancing the collectability of ash particles. Little experimental evidence is available for control of hydrocarbons or CO emissions by fuel additives, although theoretical considerations suggest that some degree of control might be possible. Practical considerations and other possible limitations to the use of additives are also reviewed.

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COMBUSTION ADDITIVES FOR POLLUTION CONTROL --
A STATE-OF-THE-ART REVIEW

by

H. H. Krause, L. J. Hillenbrand,
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SUMMARY

INTRODUCTION

The use of fuel additives for the purpose of gaining some performance advantage in fossil-fuel fired boilers has been of recurring interest for many years. Trials with various fuel additives, usually used in small amounts, have had different objectives, depending on the type of fuel involved and the era in which they were conducted. Earlier additive trials and laboratory investigations were aimed at reducing the build-up of deposits on heat-transfer surfaces and minimizing the corrosion that resulted from the accumulation of the deposits and from their interaction with the flue gases. More recently, some of the emphasis has shifted to the possible use of fuel additives as a means of controlling air-pollutant emissions -- mainly visible smoke, particulate, sulfur compounds, and nitrogen oxides.

While qualitative observations and commercial claims for the effectiveness of fuel additives in reducing emissions are numerous, relatively few quantitative data are available from experimental investigations in which conditions are well defined and in which emissions are measured. It is the purpose of this report to review the state-of-the-art of fuel additives for oil and coal firing, based on published technical literature, and to assess (as current understanding permits)

the theoretical basis for additive action in reducing the formation or emission of pollutants.

BACKGROUND OF EPA INVESTIGATIONS

The Environmental Protection Agency (EPA) has completed two of the more comprehensive experimental programs that have contributed quantitative information on the effects of fuel-oil additives in reducing pollutant emissions. One EPA program^{(1)*} covered screening tests of numerous additives in which distillate heating oil was fired in a residential oil burner. In general, the additives were found to have minor effect compared to the opportunity for emission control by burner adjustments. The second EPA program⁽²⁾ was an investigation of the effectiveness of several proprietary fuel-oil additives in reducing sulfur oxide emissions when firing residual oil in a commercial boiler. No effect was found for sulfur oxides or the other gaseous pollutants.

A third and current program, of which this review is an initial part, was conducted at Battelle-Columbus Laboratories under contract with EPA to investigate the effects of combustion-type fuel-oil additives on particulate emissions and on particulate composition⁽³⁾. Additives for experimental evaluation under this program were selected on the basis of this state-of-the-art survey and analysis.

CLASSIFICATION OF POLLUTANTS AND FUEL ADDITIVES

Pollutant Classes

In considering the effects of additives on pollutant emissions, it is useful to classify the pollutants as follows:

* References are listed at the end of this report.

- Products of "incomplete combustion (Fuel-derived species capable of further reaction with oxygen, such as CO, hydrocarbons, polycyclic organics, "carbon" particulates, or soot).*
- Nitrogen oxides from thermal fixation of nitrogen.
- Nitrogen oxides formed from chemically bound nitrogen in the fuel.
- Elements present in the fuel which are considered pollutants regardless of the form in which they are emitted. (Heavy metals, chlorine, sulfur).
- Ash components other than those included above (Fly ash).

The first three of these pollutant classes are the result of some chemical reaction (or lack of some reaction) of the fuel, air, or air and fuel. Thus, one might hope to find an additive which would influence the chemical reactions in such a way as to minimize the creation of, or maximize the destruction of, these pollutants. Such an influence is not possible for the last two pollutant classes which are considered pollutants regardless of their chemical form. At best, one could only hope to retain the pollutant within the combustion system for later removal or promote its removal and retention by some downstream control device. In assessing the use of additives to control pollutants, it is important to keep in mind the importance of not replacing one problem with a new one, such as undesirable emissions resulting from the additive constituents.

Additive Classes

Fuel additives have been used as a means of accomplishing a number of functions. These functions can be distinguished by whether they occur before, during, or after the combustion process, and the additives classified accordingly. Table 1 outlines specific functions of additives in each of these three classes:

* Emissions of polycyclic organic matter (POM) are of concern because of the carcinogenic nature of some compounds in this class⁽⁴⁾.

- Class I. Fuel-Handling Additives
 Class II. Combustion Additives
 Class III. Post-Flame Treatment Additives.

Class I additives may in some circumstances contribute to the control of pollutant emission through their influence on the physical properties of the fuel or by stabilizing the condition of important fuel-handling elements; for example, maintaining spray nozzle cleanliness. However, such effects are incidental and can be expected to be small in the presence of proper fuel handling and equipment maintenance.

Class II additives are specifically intended to affect the combustion process and, hence, may have a direct influence on the pollutants classed as products of incomplete combustion. These additives are often termed "combustion improvers".

Class III additives that operate in the post flame region include various scavenging agents and pollutant property modifiers, as well as agents which modify the catalytic properties of exposed heat exchanger and breeching surfaces.

TABLE 1. CLASSES OF ADDITIVES BY FUNCTION IN OIL AND COAL COMBUSTION SYSTEMS

CLASS I. <u>FUEL-HANDLING ADDITIVES</u> For Improved Storage and Handling	CLASS II. <u>COMBUSTION ADDITIVES</u> For Improved Combustion and Pollutant Reduction	CLASS III. <u>POST-FLAME TREATMENT ADDITIVES</u> For Post-Flame Treatment
Fuel stability additives - Sludge and gum inhibitors - Detergents - Metal deactivators - Color stabilizers Flow improvers - Pour-point depressants Demulsifying agents Anti-static additives Anti-icing compounds Corrosion inhibitors (for tank protection)	Combustion improvers - To reduce smoke or particulates - To reduce CO, hydrocarbons, or polycyclic organic matter Additives to alter particulate size or character Additives to reduce formation of pollutant gases - Nitrogen oxides, NO _x - Sulfur trioxide, SO ₃	Soot removers (from heat-transfer surfaces) Additives to control fireside corrosion or slag deposits Additives to enhance particulate collection in electrostatic precipitators SO _x scavengers

SCOPE OF REPORT

The state-of-the-art study covered in this report was directed toward additives of Class II, plus those of Class III that are added with the fuel or are added separately to the combustion chamber and that may function to control pollutant emissions from oil-fired and coal-fired boilers.

No attempt is made to cover the incidental effects of Class I additives, as such effects (when they exist) are almost totally dependent on equipment design and condition. Also, no attempt is made to review the literature concerning additions of water in sprays or in emulsified fuels, or addition of limestone, as in the dry limestone SO_2 control process. With these exceptions, consideration includes all materials (other than substitute fuels) which are added to a fuel or to the combustion chamber with the intended result of reducing pollutant emissions by any mechanism.

In addition to information on additives in fuel oil and coal combustion, data relative to other fuels are included where additive performance has been recorded. The main emphasis is on fuel additives applicable to firing boilers; however, some data on additive effects on emissions from gas turbines and reciprocating internal-combustion engines are included where these appear possibly pertinent to combustion in boilers.

This state-of-the-art review is based on information available in published technical literature.* The report is divided into two complementary parts:

* Results from the current experimental investigation, conducted as part of this contract, are to be covered in a separate report.⁽³⁾ Also included in the appendix to that report is a review of Class I fuel-handling additives.

Part I. Analysis of Combustion Mechanisms.

This part comprises a review of combustion mechanisms as they relate to the chemical basis for emission control by combustion additives.

Part II. Review of Experimental Additive Investigations.

This part reviews specific investigations reported in the literature with respect to the effect of fuel additives on emissions of one or more of the following pollutants:

- Particulate and smoke
- Polycyclic organic matter (POM)
 - of interest because of the carcinogenic nature of some of these materials
- Sulfur oxides
 - including the corrosive effects of SO₃ emissions
- Nitrogen oxides.

In part II, 43 literature references are cited, in which 58 different additive compounds have been identified and in which some quantitative data have been reported as to their effects on pollutants.

OVERVIEW AND CONCLUSIONS

The conclusions reached by this overall review are discussed below by the category of pollutants, followed by general comments on the use of fuel additives; then, recommendations are presented relating to further R&D needed to fill gaps in information. Although a number of possibilities for advancing the state-of-the-art are suggested, with few exceptions, the probability of a successful and practically useful outcome for emission control is relatively low, compared to opportunities for improvements by good combustion design and practice.

The following overview summarizes principal conclusions on combustion-type fuel additive effects as related to:

1. Products of incomplete combustion.
2. Emissions resulting from fuel impurities.
3. Emissions of nitrogen oxides.
4. Boiler efficiency.

Also, for sake of perspective, possible limitations to the use of fuel additives are discussed in a fifth section.

1. ADDITIVE EFFECTS ON PRODUCTS OF INCOMPLETE COMBUSTION

Products of incomplete combustion include CO, hydrocarbons, POM, smoke or soot, and coke particles. This class of pollutants offers perhaps the most fertile field for additive application. Recorded research is limited to "particulates" (i.e., smoke or soot and coke particles, and POM), although one might expect additives affecting any of the products of incomplete combustion would have detectable effects on the others. Obviously, the ash portion of the particulate emission (or fly ash) can not be reduced by an additive; however, the combustible or carbon portion can be reduced.

Effects on Combustible Particulates

The greatest effort in fuel additive studies has been devoted to particulate and smoke emissions. For minimizing particulate formation in fuel-oil combustion processes, experimental evidence shows that the most effective agents are compounds of some transition metals (manganese, iron, nickel, and cobalt) and some alkaline-earth metals (barium and calcium). Organometallic derivatives of these metals have given the best results. The organic portion of the molecule provides the needed solubility in the oil, while also influencing the stability and volatility of the additive molecule.

It is generally proposed that the transition metals catalyze the oxidation of soot in the hot combustion gasses. Of the alkaline-earth metals, barium has been suggested to act as a catalyst for the decomposition of hydrogen and water, promoting the destruction of soot by the free radicals thus generated.

No research clearly pertaining to coke-particle emissions was found. While it may reasonably be assumed that the same type of additives effective in reducing smoke or soot emissions will be effective in reducing coke particle emissions, the optimum additive volatility or thermal stability may differ. A possibility exists for the application of selected cracking catalysts to inhibit coke formation from heavy oils.

Finally, questions concerning electrical effects in smoke formation and their relation to the effectiveness of some types of additives have not been resolved. Systematic research with additives selected or designed to produce specific flame ionization levels would be needed to explore this point.

Effects on Polycyclic Organic Matter (POM)

Polycyclic organic matter (POM) comprises a class of potentially hazardous pollutants generally resulting from incomplete combustion (4). This class includes (1) polynuclear aromatic hydrocarbons, commonly identified in the literature as PNA or PAH, and (2) nitrogen-containing heterocyclic compounds.

Only a few investigations have reported the effects of additives on POM emissions, and much of this research has been directed toward diesel engines rather than boiler applications. Thus, the reported effects of such additives as nitroparaffins, nitrate esters, organic peroxides, etc., may have limited meaning in boiler combustion. Also, it should be recognized that most of the investigations reporting on POM were published 5 or 10 years ago; the techniques of collecting and analyzing POM have advanced considerably during that time and are still being developed.

Although the physical state of POM and soot are different, their probable common ancestry and chemical reactivity suggest that an additive effective for one would be at least somewhat effective for the other. This conjecture is generally supported by the experimental evidence, but with one interesting exception: an "oil-soluble barium compound", moderately effective in reducing diesel smoke, was reported as having no effect on POM. If, in fact, barium functions as a free-radical promoter, one would expect it to be particularly effective in reducing POM as compared to the post-flame oxidation catalysts, such as the transition metals are believed to be. However, if one accepts the conjecture that an oxidation catalyst-type additive that is effective in reducing soot would also be effective in reducing POM, there still is no reason to assume that the optimum additive stability and volatility would be the same for both pollutants.

While an additive that reduces particulate may affect some reduction in POM emissions, there is a need for additive investigations specifically directed to POM control.

Effects on Carbon Monoxide and Hydrocarbons

CO and hydrocarbons are significant pollutants, but their emission levels are usually relatively low from continuous combustion systems like boilers; consequently, few investigations have been reported on the effects of additives on these pollutants from boilers. Generally, the oxidation-catalysts effective in reducing soot or, especially POM, might be expected to have some effect on CO and hydrocarbon emissions. In view of the relative unimportance of these emissions from boilers, investigation of this aspect does not appear to be justified.

2. ADDITIVE EFFECTS ON EMISSIONS RESULTING FROM FUEL IMPURITIES

The fuel impurities considered here are sulfur and ash. These impurities are considered pollutants regardless of the form in which they are emitted.

Effects on Sulfur Compounds

Mechanistically, no fuel additive can be expected to have a direct effect on the emission of sulfur present in the fuel. Most of the sulfur in the fuel leaves the system as SO_2 (assuming that the combustion is not unusually fuel rich). Typically, only 1 to 3 percent of the sulfur leaves the system as SO_3 , depending on combustion conditions. In addition, emissions can include particulate sulfates.*

* It may be noted that some additives may change the chemical or physical form of the sulfur emissions to one that is not detected by the sampling and analytical techniques commonly used to determine SO_2 or SO_x emissions.

Various fuel additives, mostly basic in character, have been used to scavenge SO_3 or, used in much larger amounts in downstream addition, to scavenge SO_2 . (This reaction with SO_2 is typically incomplete, and the additive must be used in quantities substantially greater than the stoichiometric amount to achieve high reductions.) It is possible that an additive could be found that would promote the reaction of SO_2 with basic materials; the reported ability of sodium chloride to enhance the absorption of sulfur oxides by the limestone in fluidized-bed coal combustors suggests that such effects exist. However, the large quantity of basic material required, even if used stoichiometrically, still may limit any practical application in ordinary combustion systems.

Effects on Ash

Additives may change the physical properties of ash, but an additive cannot be expected to reduce the combustion generation of ash from constituents contained in the fuel. However, ash collectability may be influenced. SO_3 and other conditioners are sometimes added in the post-combustion zone to reduce the resistivity of fly ash, and thus promote its collection in electrostatic precipitators. There may also be an opportunity of accomplishing this conditioning through the use of compounds (other than sulfur) added to the fuel.

3. ADDITIVE EFFECTS ON NITROGEN OXIDES

Nitrogen oxide emissions are attributed to two sources: thermal fixation of nitrogen and the oxidation of organically-bound-nitrogen compounds in the fuel. The reported examples of additives causing significant (though not major) reductions in NO_x emissions seem more puzzling than illuminating. The mechanisms by which the observed effects could have been produced are obscure.

Effects on Thermal-Fixation Processes

The importance of O- and N-atom levels in the mechanism for the fixation of nitrogen suggests that additives which might reduce, principally, the concentration of O-atoms could be effective in reducing NO_x . In practice, additives have not been especially effective in this regard. One of the problems is that hypothetical additives which might reduce the O-atom level by promoting atom recombination reactions, or by retarding the combustion reactions leading to O-atom formation, could be too detrimental to the overall combustion process.

Effects on Fuel-Nitrogen Conversion

NO_x is formed more readily from chemically-bound-nitrogen species than from the fixation process. To reduce NO_x from fuel-N species requires that the decomposition of the fuel-N be diverted to N_2 or N_2O , rather than active CN or NH species. No additives have been found which accomplish this. Interestingly, however, there is evidence that NH species can limit, and perhaps reduce, the conversion efficiency of fuel-N compounds to NO.

On the basis of the information available, it is possible that some minor degree of NO_x control may be obtained with fuel additives; the probability of practical success, however, still appears questionable.

4. ADDITIVE EFFECTS ON BOILER EFFICIENCY

Two routes are open to influence boiler efficiency by fuel or combustion additives: (1) through cleaning or maintaining the cleanliness of heat-exchanger surfaces, or (2) by controlling pollutants, particularly visible smoke, thus permitting operation at reduced excess-air levels. Additives intended to remove or modify soot and other surface deposits have a significant history but are outside the scope of this report. However, additives which suppress smoke (soot) and other carbon

particulate may both reduce the rate of fouling of the heat-exchange surface and permit operation at lower excess-air levels. The possible efficiency gain depends on the smoke-limited excess-air level of the specific burner-boiler combination, its normal rate of fouling, and the frequency of cleaning. Efficiency gains of a few percent may be possible in small boilers which are reasonably maintained and adjusted⁽³⁾. In larger boilers, with well-designed fuel-air mixing, equipped with soot blowers and possibly heat-recovery equipment, and subject to skilled maintenance and adjustment, additives offer little promise of efficiency gains.

5. POSSIBLE LIMITATIONS TO THE USE OF ADDITIVES

A perspective of the potential use of fuel additives for control of air-pollutant emissions from oil-fired and coal-fired boilers should include these additional considerations:

- Combined emission impact, including effects of the additive on various pollutants.
- Possible toxic effects of trace pollutant emissions resulting from materials introduced with the additives.
- Effects of equipment characteristics on fuel additive effectiveness.
- Practical considerations of additive use, other than simply the reduction of one or more pollutants.
- Comparison of the effectiveness of additives with alternative control means.

Each of these possible limitations is discussed in the paragraphs below.

Overall Emission Impact

The overall or net impact of a fuel additive on a number of different pollutants must be considered in combination, so that means for

solving one pollutant problem do not create another problem by bringing about an increase in another pollutant. For example, some additives may affect reductions in one pollutant but increase the emission of another pollutant. Fortunately, most additives which have been shown effective in reducing pollutants that result from incomplete combustion are not expected to adversely effect other criteria pollutants.

Toxic Effects

Included in the overall consideration of additive usage is the possibility that materials present in additives may produce pollutants which are toxic. For example, metal-containing additives will result in emissions of the metal or metals, the possible adverse health effects of which must be balanced against the reduced emissions of the target pollutant. In many cases, the potential adverse effects of such emissions are not adequately understood.

The Effect of Equipment Characteristics on Fuel Additive Effectiveness

In the case of fuel impurities (such as sulfur and heavy metals) and the nitrogen oxides, the evidence for additive effectiveness is too uncertain and the possible modes of action too obscure to permit any rational discussion of how their effectiveness may be influenced by equipment characteristics.

In the case of products of incomplete combustion, especially carbon particulates and soot or smoke, there is both experimental evidence of additive effectiveness in continuous combustion systems and reasonable conjecture as to how the additives function. Consequently, for additives effective in reducing smoke and carbon particulate, some consideration of the influence of equipment characteristics, or combustion conditions, is possible. Such influences may explain the varying degrees of effectiveness found for the same or similar additive by different investigators. Following are some examples of equipment characteristics that may influence additive effectiveness.

Effects of Fuel-Air Ratio. It is easy to conceive that fuel-air ratio may affect the performance of additives intended to control emissions of products of incomplete combustion, since, in the extreme case of sub-stoichiometric air, combustion must be incomplete regardless of additive effectiveness. The suggestion that barium functions as a free radical promotor and is thus active in the high-temperature region of active combustion, while the transition metals catalyze or accelerate the oxidation of solid carbon in the post-flame region, has been proposed as an explanation for an observed difference in the effectiveness of these additives at differing fuel-air ratios. Thus, the effectiveness of barium in suppressing smoke was little affected by the overall fuel-air ratio, while the effectiveness of the transition metal manganese was observed to decline with excess air.

Effects of Time-Temperature. The belief that the transition metals are active in the post-flame region also suggests that their effectiveness may be influenced by the rate of heat extration from the combustion products. If the combustion space is small and the combustion products are cooled rapidly, additives that are intended to catalyze oxidation of the carbon particles would be relatively ineffective. Such rapid post-flame cooling would have a lesser effect on the action of barium or, assuming a similar basis of action, the other alkaline earth metals which function in the combustion zone. In contrast, low combustion temperatures such as accompanying two-stage or distributed combustion, might reduce the effectiveness of the alkaline earth metals without greatly affecting the activity of the transition metals.

Effects of Fuel Vaporization and Fuel-Air Mixing. The possibility exists for the fuel additive to be separated from the region where its activity is needed. Thus, an additive retained in a coke or ash particle would be ineffective in reducing smoke emissions. Likewise, smoke formed during the initial burning of the fuel might be little affected by an additive released from the liquid fuel at a latter stage of the combustion process. Separations such as these, or their reverse,

will be influenced by the volatility and thermal stability of the additive, the character of the fuel, and the thermal regime characterizing the vaporization zone of the equipment.

At the moment, the above descriptions of possible influences of equipment types on additive effectiveness must be regarded as providing a basis for anticipating such influences rather than being definitive examples. Experimental investigations under controlled conditions will be required to identify the parameters of importance for various equipment and additive types.

Other Practical Considerations

Practical considerations that may limit the feasibility of additives include possible effects on (1) storage stability* and handling characteristics of specific fuels, or (2) deposits in burner parts or flue passes. Such effects may not be easily predictable without investigation of additives under specific field conditions to be encountered.

Alternative Controls

Other alternative means of emission control may be more effective than the use of additives in many situations. Both practical effectiveness and cost effectiveness should be considered. For example, burner design and adjustment for the desired fuel-air mixing condition and thermal environment generally can reduce emissions resulting from incomplete combustion. However, where conditions are marginal and are not subject to sufficient improvement, additives may have application for control of those emissions resulting from incomplete combustion. A similar interaction may result from combustion modifications (such as

* Storage stability includes such aspects as sediment and gum formation (especially moisture sensitivity).

staged combustion) intended to control nitrogen oxides. If it should develop that such modifications lead to excessive emissions of products of incomplete combustion, especially soot, fuel additives may offer a route to overall emission control. At present, this possibility has not been sufficiently investigated.

In short, the needed perspective must include consideration of the full spectrum of pollutants and control alternatives applicable to each type of boiler installation.

RECOMMENDATIONS FOR FURTHER R&D

This review has demonstrated that there is some evidence, experimental and theoretical, regarding control by fuel additives of most pollutants emitted by combustion systems. The evidence for control by fuel additives of visible smoke and carbon particulate is strong, for control of POM is somewhat weaker, and for control of NO_x is quite weak (except by ammonia as a Class III additive). Control of total sulfur emissions by additives does not appear to be possible; emissions of SO_3 can be controlled, although the equivalent amount of sulfur may still be emitted as a solid sulfate salt. Possibilities for the control of emissions of ash or specific ash constituents by fuel additives is restricted to enhancing the collectability of ash particles. No experimental evidence is available for control of hydrocarbons or CO emissions by fuel additives, although theoretical considerations suggest that some degree of control might be possible.

In assessing the need for further investigation of fuel additives, the importance of the specific pollutants must be considered, as well as alternative control techniques. Hydrocarbons and CO are not usually important pollutants from continuous combustion sources. NO_x and SO_x are important pollutants, but there is little evidence to suggest that they can be practically controlled by fuel additives. But SO_3

emission can be controlled by additives, and this control may be significant in terms of local air quality. Additional research appears to be needed to clarify the role of SO_3 emission relative to total sulfur emission and emission of SO_3 as solid sulfate salts. Carbon particulates and visible smoke are important pollutants, but may be more easily controlled by proper equipment design and operation. Ash, appearing as fly ash, is perhaps a special case in that combustion additives or post-flame additives may enhance the collectability of the ash and thus aid the control of this emission by other methods.

On the basis of these considerations, the most promising area for further R&D on combustion additives is the control of carbon particulate and related pollutants (such as visible smoke and POM), wherein modest increases in boiler efficiency can be an added benefit. Three specific investigations can be suggested beyond the current EPA/Battelle laboratory evaluation of combustion additives for fuel oil. These three studies involve field and laboratory investigations of the effectiveness of combustion-type fuel additives in controlling carbon particulate and visible smoke from:

1. Different types and capacities of boilers within the intermediate size range firing residual oil.
2. Boilers firing oil or pulverized coal where combustion modifications for NO_x control are employed.
3. Coal burning in stoker-fired boilers ranging in size from small-commercial to small-industrial.

The first of these suggested investigations is intended to assess the practicality of using residual-oil additives for emission control for a variety of boilers under field conditions and oil types. (Additives may offer a practical means of particulate control for residual oil-fired boilers in an intermediate range of commercial/industrial sizes, typically used in applications where burner maintenance is marginal and which are too small for high-efficiency collectors to be used economically.) The second investigation would explore the potential of additives

in particulate control where combustion modification for NO_x control yields conditions that are conducive to the formation of carbon particulate. The third investigation would explore the technical feasibility of controlling emissions from small commercial coal-burning equipment that may not be equipped with high-efficiency collectors.

Depending on the importance attached to SO_3 emissions, as contrasted to total sulfur emissions, research to determine the mode of action of known SO_3 suppressants (i.e., prevention of SO_3 formation or scavaging of SO_3 to form sulfate salts) may be justified.

Throughout this review, attention is called to possible research of a fundamental nature directed towards improving the performance of additives, finding new classes of additives, and explaining the mode of action of additives. The possibility that this research would ultimately result in new or more extensive applications of additives for emission control is regarded as relatively remote. Consequently, insofar as the interest in additives is practically directed, these more fundamental research opportunities would be assigned a lower priority than field and laboratory trials to assess the use of additives over a range of burner-boiler types, sizes, and operating conditions

* * * * *

Detailed discussion and other background information that supports the foregoing Summary are contained in the following parts:

- Part I. Combustion Mechanisms as They Relate to Fuel-Additive Action in Controlling Emissions
- Part II. Review of Experimental Investigation of Combustion-Type Fuel Additives

PART I

COMBUSTION MECHANISMS AS THEY RELATE TO FUEL-ADDITIVE ACTION IN CONTROLLING EMISSIONS

The combustion of fuels for the generation of heat is ordinarily an efficient process, and the available heat of combustion which is lost in the form of incompletely burned fuel is generally insignificant. However, it is now recognized that these small quantities of incompletely burned fuel, as well as emissions resulting from certain fuel impurities and high temperature nitrogen fixation, are extremely significant as air pollutants. This recognition has resulted in considerable research directed towards gaining an understanding of how and why these pollutants are formed, with the hope that such understanding will lead to methods of preventing their formation or of destroying them during the combustion process.

POLLUTANTS CATEGORIZED BY ORIGIN

In terms which reflect both their source and the possible methods of control, the pollutants emitted from combustion processes can be categorized as follows:

- Chemical species derived from incomplete combustion of the fuel and capable of undergoing further reaction with oxygen. These species include CO, "Carbonaceous particulates" such as soot or coke particles, "hydrocarbons", and polycyclic organic matter or POM.

- Nitrogen oxides resulting from the thermal fixation of atmospheric nitrogen.
- Nitrogen oxides resulting from the oxidation of chemically bound nitrogen in the fuel.
- Compounds of toxic elements, such as sulfur and heavy metals, resulting from the presence of these elements in the fuel.
- Mineral particles formed from the mineral matter or ash present in the fuel.

It is immediately clear that if the emission of an element is regarded as undesirable regardless of its form, and that element is present in the fuel, then nothing can be done in terms of the combustion process that will avoid its release. The best we could hope for would be to retain the element in the combustion system for later disposal rather than emitting it into the atmosphere.

As an example, sulfur in fuel is ordinarily emitted as SO_2 together with a small amount of SO_3 . Presumably one might (and sometimes does) alter the combustion conditions to favor one or the other of these oxides, but emissions of either are regarded as undesirable. By drastic alterations of the combustion process, the sulfur might be converted to species such as H_2S , CS_2 , etc., but emissions of these species are unlikely to be regarded as an improvement. Finally, one might add substances to the fuel which will react with the sulfur oxides, such as sodium carbonate or limestone, forming solid sulfates and sulfites. Although less noxious than the sulfur oxides, indiscriminate emissions of such salts add to the particulate loading of the atmosphere, and hence, it is important to collect these solids from the stack gas and dispose of them in some unobjectionable manner.

The same situation pertains to either fuel "impurities" and ash-forming matter. The situation is, however, different for the first three pollutant categories listed above. All of these are characterized as being nonequilibrium species in the sense that they would not be expected to exist in significant quantities in a homogeneous fuel-air mixture which passed through the observed temperature profile while maintaining continuous chemical equilibrium. Hence, their existence suggests that either the fuel-air mixture was not homogeneous, or that continuous chemical equilibrium was not maintained.

When viewed in sufficient detail, combustion processes always prove to have some degree of inhomogeneity: at the least, some region containing a composition, temperature, or velocity gradient must exist to stabilize the flame. In practical combustion processes, other inhomogeneities may exist due to the nature of the fuel (e.g., heavy oils and coal) or may be deliberately introduced to control the nature of the flame (e.g., luminous or nonluminous) or the heat release pattern. However, the design of practical combustion systems attempts to achieve homogeneity at some point within the combustion system. If this condition is not achieved, or is achieved after the gases have been cooled to too low a temperature, then possible routes to the emission of various combustible pollutants can easily be visualized. Thus, if a flow path exists which is never subjected to the conditions needed for ignition of the fuel, or which never contains enough oxygen for the complete combustion of the fuel, then species such as hydrocarbons, CO, soot, etc., may become equilibrium species for that path. Some mechanism of this type is often suggested as a source of hydrocarbon and CO emissions from the reciprocating internal-combustion engine. Such emissions represent not so much a "failure of chemistry" as a failure of design.

Perhaps more typical of practical combustion processes is the case where a sufficient degree of homogeneity is achieved (either by preflame or postflame mixing) but at a temperature too low or, for a time, too short to permit the desired chemical reactions to proceed to completion. The chemical reactions are quenched and equilibrium is never achieved.

The following section within Part I of this report considers the mechanisms of formation for major pollutants. In the succeeding section, the mechanisms for the various pollutants are discussed as they relate to opportunities for fuel additive action in controlling emissions.

MECHANISMS OF POLLUTANT FORMATION IN COMBUSTION PROCESSES

The oxidation of hydrocarbons in flame is a complex process accompanied by the formation and subsequent destruction of many intermediate products. Thus, proposed reaction schemes for the burning of methane with oxygen may include at least 12 species without considering minor species containing more than one carbon atom. For methane, the reaction scheme is, in outline^(5,6):



resulting from pyrolysis, or attack by O, H, or OH:



which results from reaction with O or O₂:



through reaction with OH or thermal decomposition, followed by:



The oxidation of more complex hydrocarbons is usually considered to proceed in a roughly comparable way.

PRODUCTS OF INCOMPLETE COMBUSTION

Carbon Monoxide

The first important feature of this scheme is that the formation of CO is an unavoidable step in the oxidation of the carbon to CO₂. The second important feature is that CO is oxidized or destroyed by reaction with hydroxyl radicals.

The significance of these two features is first, that one cannot expect to avoid the formation of some CO when burning a hydrocarbon (or generally, any organic compound), and second, that the destruction of CO by the normal route (i.e. reaction with hydroxyl) may be a marginal process. This second point results from the fact that the concentration of hydroxyl is strongly temperature dependent: if the CO-containing gas is rapidly cooled, the hydroxyl concentration may drop to insignificant values before the CO is oxidized, regardless of the availability of oxygen.

Hydrocarbons

The emission of the materials normally labeled "hydrocarbons" from combustion processes in which a reasonable degree of homogeneity is achieved is difficult to explain, if for no other reason than the fact that with a few exceptions these materials are not well characterized. Of course, "hydrocarbons" are not usually important combustion-derived pollutants other than from systems well known to

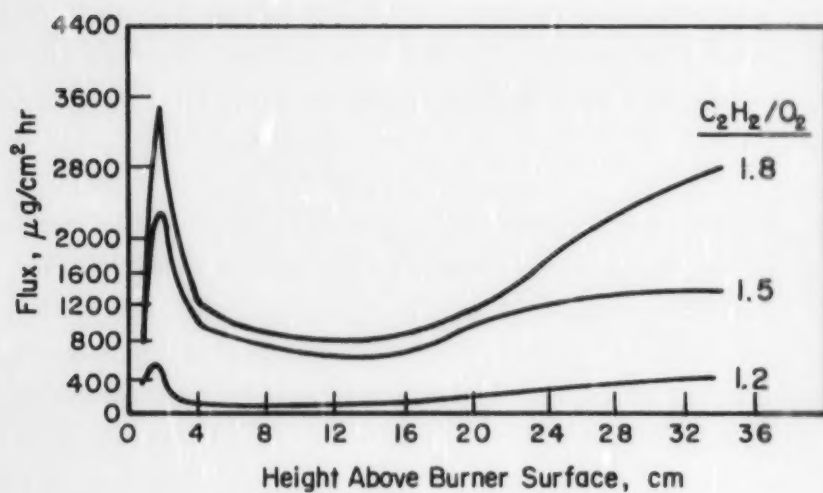


FIGURE 1. FLUX OF POLYCYCLIC AROMATIC HYDROCARBONS VS HEIGHT AND BURNER SURFACE (from Reference 9)

possess important quenching effects or inhomogeneities, such as the reciprocating engines and aircraft gas turbines, or which undergo repetitive transients, such as the off-on cycle of automatic home heating equipment ⁽⁷⁾. If "hydrocarbons" are emitted other than by the above processes, one might expect that they result from quenching the combustion process at a point where significant quantities of "organic" carbon remain, as hydrocarbon radicals, aldehydes, etc., with subsequent stabilization by recombination, polymerization, etc.

Polycyclic Organic Matter

Materials labeled polycyclic organic matter (POM) are emitted from combustion systems in small quantities. POM is defined to include polycyclic aromatic hydrocarbons (PNA or PAH), nitrogen-containing heterocyclic compounds, and possibly derivatives of these ⁽⁴⁾. Studies of the mode of formation and destruction of POM in the combustion process are difficult to carry out because of the very low concentrations, the lack of simple analytical procedures for identifying them, and the large number of individual compounds making up this class of material.

Studies of rich acetylene and ethylene flames strongly suggest that POM is formed through the polymerization of a two-carbon radical, probably acetylenic, and is probably destroyed by some reaction involving hydroxyl ^(8,9). The two-carbon radical is not necessarily derived directly from the fuel, but rather may be built up from single carbon fragments.

Figure 1 illustrates the observed flux of POM in rich, low-pressure acetylene-oxygen flames ⁽⁹⁾. Evidently POM is formed rapidly in the initial part of the flame, and much of this is destroyed in the highest temperature region. However, a secondary process of formation occurs as the temperature of the burned gases drops into the range of

650-900 C. The fact that POM exists and is even created under such conditions is indicative of the extreme thermal stability of the polyaromatic structure.

It may be noted that the POM flux becomes very small as the fuel-oxidizer ratios approach stoichiometric, even though the mixture is still very fuel rich.

Some fuels contain POM as a constituent. Specifically, coal might be regarded as being largely POM, and if combustion conditions are such that insufficient temperature or oxidant concentration is encountered by the fuel-POM, this source may dominate the emissions. In fact, large emissions of POM have typically been associated with hand-fired coal furnaces, burning coal mine waste, and other poorly controlled combustion systems⁽¹¹⁾.

Soot

Soot, or loosely, smoke, was probably the first combustion-generated air pollutant to be recognized and, consequently, has received considerable research effort. Nevertheless, soot remains, perhaps, the least understood of all the combustion-generated pollutants. Soot is formed both by reactions in flames and by pyrolysis of organic carbon species. It has long been recognized that the emission of soot represents incomplete burning of the fuel and that the ample provision of air and maintenance of high temperatures decreased the quantity of or eliminated the soot.

With the introduction of petroleum-based fuels, it was found that various hydrocarbons had differing soot-forming tendencies. Thus, in the smoke lamp, it was found that the various hydrocarbon types could be rated in terms of smoke-forming tendency as: paraffins < naphthenes < olefins < monocyclic aromatics < polycyclic aromatics⁽¹²⁾.

It has also been found that the dilution of the fuel or air or their mixture with inert gases, steam, carbon dioxide, or cooled flue gas tended to suppress the formation of soot⁽¹³⁾. Water sprays directed into the flame and firing water/oil emulsions⁽¹⁴⁾ have also been found to suppress the formation of soot. The mechanisms behind these phenomena have not been resolved.

Examination of soot particles with the electron microscope has revealed that the large, visible particles were agglomerates of small spherules with diameters in the range of 10 nm. X-ray diffraction studies showed the presence of graphite crystallites^(6, 12).

In spite of this long history of research, and the discovery of methods of controlling at least partially the emission of soot from combustion processes, soot remains an important pollutant for numerous small combustion systems^(15, 16)

It is probably incorrect to consider soot as only carbon; chemical analysis typically reveals the presence of hydrogen in non-negligible quantities. Moreover, it has been found that soot may contain significant quantities of POM and other hydrocarbons that can be extracted by solvent or vaporized in a vacuum. In some soots, the POM may exceed 3 percent by weight⁽⁸⁾.

In view of the graphite structure observed in soot, its hydrogen content, and the simultaneous occurrence of soot and POM, it is possible to conceive of soot as POM carried to an extreme. Indeed, various studies have indicated a probable origin of soot in the two-carbon fragments found in flames, and the flux of soot or soot precursors in rich acetylene flames has been found to be very similar to the flux of POM^(8, 9, 17).

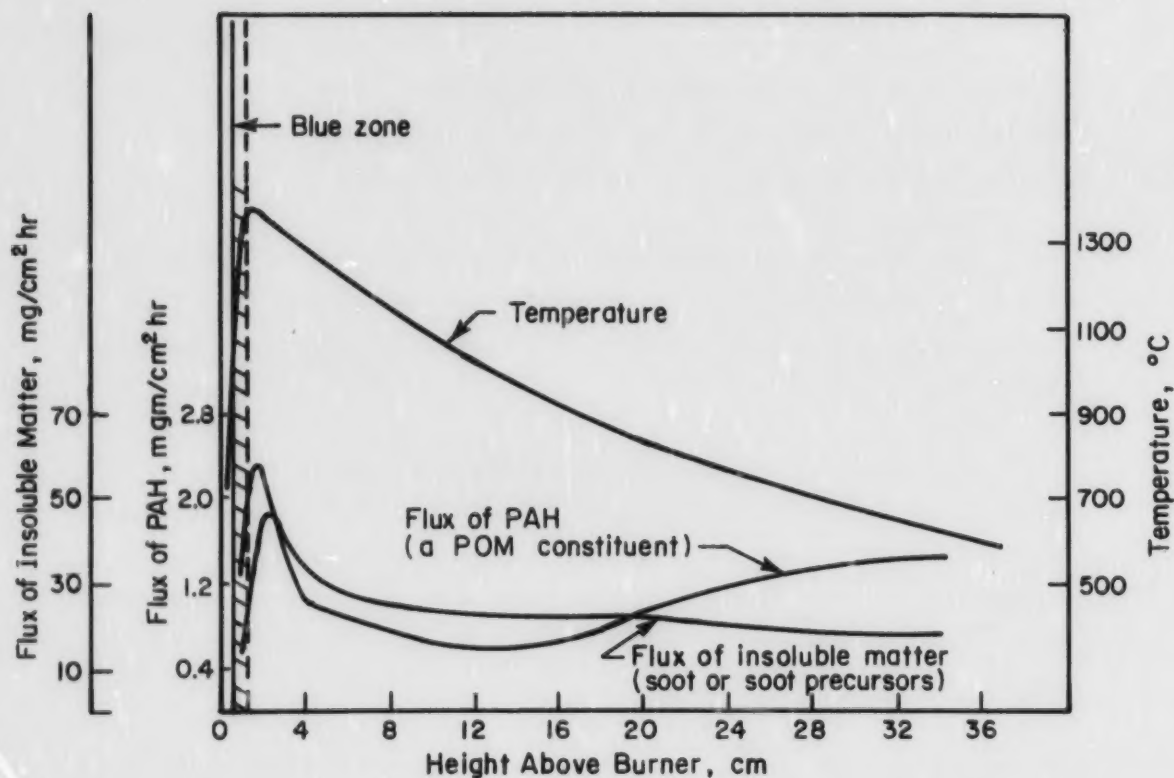


FIGURE 2. COMPOSITE PLOT OF FLUX OF INSOLUBLE MATERIAL (SOOT), FLUX OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) AND OF TEMPERATURE, RESPECTIVELY; VERSUS HEIGHT ABOVE BURNER SURFACE IN A RICH, LOW-PRESSURE ACETYLENE-OXYGEN FLAME (from Reference 9)

Figure 2 illustrates this parallelism⁽¹⁰⁾. It has been suggested that the oxidation of soot depends primarily on OH⁽¹⁸⁾, although suggestions have also been made that oxidation by O atoms is important or even dominates^(6, 19). The strong pro-soot activity of SO₃ in flames has, thus, been explained as resulting from the scavenging of O atoms by the SO₃⁽⁶⁾.

The problem presented by soot differs from that of POM in at least one important aspect: soot is emitted as discrete particles, whereas the POM is emitted from the flame as a vapor. Thus, in addition to the chemical problem of its formation, the formation of soot must involve the physical processes of nucleation and growth of a new phase. Similarly, the oxidation of soot is a heterogeneous reaction involving the diffusion of species to and away from the surface.

The possibility that electric charges and fields may play a role in either the nucleation, growth, or agglomeration of soot has frequently been suggested. Evidence supporting such concepts has been obtained but this evidence does not exclude mechanisms involving neutral species^(6, 20).

Emissions of carbon from combustion systems include, in addition to soot, relatively large "carbon" particles representing an unburned residual of the original fuel particle or oil droplet. These particles are formed first by devolatilization of the fuel particle by the processes of simple vaporization and pyrolysis, leaving behind a nonvolatile residue of coke. If combustion conditions are such that the hot coke particle co-exists with vaporized fuel, heterogeneous pyrolysis reactions may lead to growth of the coke particle at the expense of the fuel vapor.

Because the pyrolysis reactions leading to coke formation occur at appreciable rates only at high temperatures, above perhaps 300 C, the formation of coke particles is usually a problem only for those fuels having constituents with low vapor pressures at such temperatures, e.g. heavy oils and coal. Because survival of the coke is dependent on its residence time in a high-temperature environment, coke-particle emissions are typically a greater problem in smaller equipment, such as commercial-size boilers, rather than in the larger industrial or utility boilers.

The amount of coke formed is dependent on the heating rate, because the pyrolytic polymerization reactions in the fuel particle proceed at a finite rate. Thus, studies of coal devolatilization at a heating rate of 1000 C/sec produced larger coke residues than did devolatilization conducted at heating rates of 10^4 - 10^5 C/sec⁽²¹⁾. The pyrolysis reactions are usually described as proceeding through formation of free radicals, chain propagation by hydrogen abstraction, fission to shorter carbon chains, polymerization to heavier materials with lower hydrogen content, and various radical destruction processes⁽²²⁾. However, molecular mechanisms, as contrasted to free radical mechanisms, have also been proposed⁽²³⁾.

Because of their large size, the burn-out of coke particles is a relatively slow process, most likely controlled at high temperatures by the diffusion of oxidant to and products from the particle surface. In parallel to the case for soot, the effective oxidant may be OH or O^(6, 18, 19), with the result that at lower temperatures the burning rate may be quite small even in the presence of substantial O₂.

EMISSIONS RESULTING FROM FUEL IMPURITIES

Fuel impurities of interest as pollutants currently include sulfur, inorganic substances which produce flyash, and various toxic elements. At the moment, sulfur oxides and "particulates" (regardless of chemical composition) are recognized as air pollutants in the sense that governmental restrictions have been applied to their emission. Although the results of future research are likely to extend this situation, as more and more gaseous or solid species are recognized as specific pollutants and subjected to individual regulation, attention here will be confined to sulfur-containing species and flyash.

Inasmuch as sulfur and metals occur in the fuel, they will be released in the combustion process regardless of the detailed mechanisms involved. Thus, they can be avoided as pollutants only by removing them at some point prior to, during, or after combustion.

Sulfur Compounds

In ordinary combustion processes (as distinct from gasification processes) sulfur may exist as either SO_2 or SO_3 . Although not well explained, the oxidation of sulfur is believed to proceed through the initial formation of SO followed by

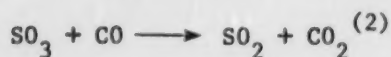


SO_2 can then be oxidized to SO_3 by the reaction



and the SO_3 destroyed by





Because SO_3 is unstable at high temperatures, some of the SO_3 initially formed by the abundance of O atoms in the flame is subsequently decomposed. As the temperature drops, SO_3 becomes more stable relative to SO_2 , but the uncatalyzed oxidation of SO_2 is slow. As a result, the concentration of SO_3 in the high-temperature region is typically observed to be much larger than the equilibrium value, while its concentration in the low-temperature region is much smaller than the equilibrium value.

Although control of the combustion process can do little or nothing about the total sulfur oxides emitted, some control can be gained over the SO_3/SO_2 ratio. This is sometimes desirable to avoid corrosion of low-temperature heat-exchange surfaces, or to avoid the formation of visible and noxious sulfuric acid mists or acid smuts (aerosols consisting of sulfuric-acid-moistened flyash and soot). In terms of combustion control, this has been accomplished in boilers by burning at low excess-air levels, such that the oxygen content of the flue gas does not exceed 0.2 percent⁽²⁴⁾. Under these conditions, the concentration of SO_3 in the flue gases appears to be substantially less than 0.1 ppm. The mechanism by which this result is obtained has not been explored. It appears likely that the formation of SO_3 in the flame zone would be unaffected, or even increased due to the higher temperature and, consequently, higher O atom concentration. Thus, decomposition of SO_3 at intermediate temperatures and suppression of the low-temperature oxidation of SO_2 by limiting the availability of oxygen are probably responsible for the low SO_3 levels achieved.

Fly Ash

The ash forming constituents of fuels are predominantly metals, although sulfur, usually as sulfate, may occur in small amounts. When present in significant amounts in the fuel, phosphorus may also be found in the ash. In coal, the original forms of the ash constituents are shales, clays, pyrites, and calcite. In oils, the quantity of ash-forming material is much less than in coals, i.e., a few hundred to a few thousand ppm in residual oil and much less in distillate oils, as contrasted to typically 10-20 percent in coal. The ash constituents in residual oil are vanadium, nickel, and possibly iron, occurring as oil soluble porphyrins; unidentified organic calcium, magnesium and zinc compounds; various clays, oxides, etc., suspended in the oil; and water-soluble salts characteristic of oil-field brines or sea water. The total ash and its composition are highly variable (25).

The detailed behavior of ash constituents during the combustion of residual oils and coals has not been investigated. Probably the various metals are converted to their oxides, if not originally present as such during burn-out of the residual coke particle. If the combustion temperature is sufficiently high, some or all of the oxides may be fused or even volatilized, to solidify and condense as the temperature falls.

In the case of coal combustion, some control of the ash properties and ash emission is possible through equipment design and operation. Thus, burning the coal in fixed-bed equipment or cyclone furnaces causes much of the ash to be retained as a solid. In pulverized-coal firing, the furnace can be designed either to fuse the ash and collect much of it as slag within the furnace, or to solidify the ash in suspension and thus carry nearly all of the ash out of the furnace with the gaseous combustion products.

In terms of chemistry, the only practically applied control of ash properties occurs in the low-excess-air burning of residual oils. Although practiced primarily for control of SO_3 , the reduced availability of oxygen causes the vanadium to form as V_2O_3 or V_2O_4 rather than the V_2O_5 characteristic at normal oxygen levels. These lower oxides are less objectionable from the standpoint of boiler corrosion.

FORMATION OF NITROGEN OXIDES

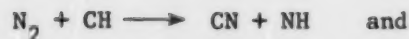
In the following discussion concerning NO_x formation, the roles of thermally fixed nitrogen and of chemically bound fuel nitrogen are treated separately.

Thermally Fixed Nitrogen

The thermal fixation of nitrogen in flames is now nearly universally attributed to the Zeldovich mechanism (26),



Reactions such as



have been suggested as important sources of "prompt NO" (that NO which is formed early in the combustion process) in flames (27). These suggestions have been challenged with the recognition that super-equilibrium concentrations of O atoms in flames could lead to the observed NO formation rates through the Zeldovich mechanism.

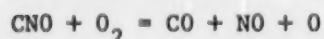
NO is not a stable species at low temperatures, and the equilibrium concentration of NO at ordinary exhaust or stack-gas temperatures is not significant. NO persists in the combustion process because of the extreme temperature dependence (high activation energy) of the reactions leading to its formation and destruction. These reactions are effectively quenched or frozen at temperatures below about 2500 F. Even moderate rates of heat removal from the combustion products will freeze the NO concentration at a value characteristic of a high-temperature equilibrium.

Although the NO concentrations in the cooled combustion products far exceed the equilibrium value, they are typically much lower than the NO concentration in equilibrium at the highest temperature achieved in the flame (possibly 3000 ppm). This results from the failure to remain at the highest temperature for sufficient time to reach equilibrium, in some situations from decomposition of the NO before the reactions are quenched, and possibly by reactions between the NO and other flame species.

Various methods of controlling the formation of NO (through Zeldovich mechanism) have been proposed. These methods are based on preventing the formation of appreciable quantities of NO through control of the peak combustion temperature. Various methods of combustion control have been investigated: dilution by flue gas through internal or external recirculation, humidification of combustion air, controlled (i.e., slow) heat release combined with heat extraction, and two-stage combustion with intermediate heat extraction. These methods have been generally successful in reducing the quantity of NO emitted⁽²⁸⁾.

Chemically Bound Fuel Nitrogen

It is well recognized that, besides the Zeldovich mechanism for explaining the thermal fixation of nitrogen, organic-nitrogen compounds in fuels are also significant sources of NO_x in combustion systems (29, 30, 31, 32). A number of recent studies have shown that fuel-bound nitrogen yields high and varying amounts of NO in combustion product gases. Fuel-bound nitrogen may be in the form of indoles, carbazoles, pyridines, quinolines, etc. Since these compounds only possess limited stability, especially in an oxidizing atmosphere, in the preflame, high-temperature gradient regions of the flame, they will break down and oxidize fairly readily. Mechanistically, the nature of the active fuel-nitrogen intermediate has not been identified. However, as these nitrogen-containing compounds and intermediates break down and oxidize, they yield a variety of NH and CN species, i.e., N, NH, NH_2 , CN, HCN, CNO, etc., which will be oxidized to NO. These species will lead to NO formation by steps such as

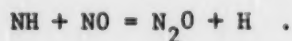


If the NH and CN species behaved strictly as indicated here, one might expect all the fuel-nitrogen species to be converted to NO. It is noted, however, that the conversion of fuel nitrogen to NO is not quantitative. Experiments (31, 33, 34, 35, 36) show that the conversion of fuel nitrogen to NO:

- decreases as the concentration of fuel nitrogen increases

- decreases as the amount of excess air is decreased (Under fuel-rich conditions, NO can be reduced to nitrogen).

To explain the nonequilibrium and "nonstoichiometric" production of NO, one must invoke reaction steps which remove or prevent NO from being formed. Two principal reaction steps generally invoked are



These steps are both thermodynamically favorable and kinetically rapid. The first of these reactions, in fact, is faster than $\text{N} + \text{O}_2 = \text{NO} + \text{O}$ under fuel-rich conditions.

POSSIBLE OPPORTUNITIES FOR ADDITIVE ACTION
IN CONTROLLING COMBUSTION-GENERATED
EMISSIONS BY FUEL ADDITIVES

Purely in terms of what may be conceived, in contrast to what may be possible or practical, the major opportunity for control of emissions by additives must be confined to those pollutants described previously as nonequilibrium species, namely, the products of incomplete combustion and the nitrogen oxides. Opportunities are much more restricted for the application of additives for control of emission of objectionable elements present as fuel impurities and of fly ash; generally, at best, one could only expect an additive to alter the physical or chemical form in such a way as to promote the removal of these pollutants in a downstream clean-up process.

In the following sections of Part I, the opportunities for additive actions are examined successively for control of

- Emissions from incomplete combustion
- Emissions from fuel impurities
- Emissions of nitrogen oxides.

CONTROL OF EMISSION FROM INCOMPLETE COMBUSTION

Perhaps the most significant feature of the combustion mechanisms previously discussed is that the global reaction



is not an elementary reaction, or reaction mechanism, of the combustion process. It is, of course, an everyday observation that fuels do not ordinarily burn simply upon mixing with air or oxygen. The real oxidants and reductants in flames prove to be radicals and fragments formed initially by thermal dissociation and oxidation steps at high temperatures and maintained and increased in concentration by chain-propagating and chain-branching reactions. The destruction of the active species by thermal or surface quenching, or by other chain-terminating events, may leave some of the fuel unconverted to the ultimate products, CO_2 and H_2O . Emissions of CO and "hydrocarbons" may result from such a sequence.

A process which could possibly complicate this situation is the existence of a fast reaction which converts reactive fuel species to products which are much less reactive with the oxidants. Combustibles could thus be protected from rapid oxidation. With the loss of heat from the combustion gases and consequent loss of the reactive oxidants, such materials could appear as stable combustion products. Soot and POM are representative of pollutants formed in this manner, and with only a slight alteration of the concept, coke particles as well.

Additives might be conceived of as altering the above sequences by one or more of the following approaches:

1. Increasing the concentration of active oxidants, providing O and OH. This might be accomplished by promoting their formation or inhibiting their destruction.

2. Introducing an active oxidant species not normally present in flames.
3. Inhibiting the formation of unreactive-combustible materials.

Each of these three approaches to reducing emission from incomplete combustion is discussed below.

1. Approach of Increasing the Active Oxidant Concentration

The concentration of O and OH in a flame or in hot combustion gases might be increased by a catalyst promoting the dissociation of, for example, H_2O , by adding a material which itself is dissociated or decomposed to yield O or OH, or by adding a material which would remove species responsible for the destruction of O and OH. None of these possibilities are considered likely of success.

The concept of increasing the concentration of O or OH in a flame (or in the still-hot combustion gases) by some catalyst would be attractive, except for the observed fact that O and OH concentrations, particularly O, exceed the thermal equilibrium concentrations not only in the flame, but for some distance downstream of the visible flame. Thus, a catalyst would be most likely to promote recombination reaction and reduce the concentrations of O and OH.

Additives which would decompose in the flame to yield O and OH appear similarly unpromising. The normal concentrations of O and OH are such that an additive would be needed in amounts comparable to the fuel if the concentrations are to be significantly increased. Finally, O and OH are capable of reacting with nearly all species present in flames, and an additive that would scavenge such reacting species would be needed in amounts comparable to the total mass of fuel and air.

The above view is entirely negative for additive control of pollutants from incomplete combustion. Nevertheless, it has been conjectured that barium functions as a smoke suppressant by catalyzing the dissociation of hydrogen and water to radicals⁽³⁷⁾. The identity of the radicals is not specified, but they could only be H and OH, with the additional possibility of O through the O₂-H reaction if O₂ is present. The evidence for this conjecture is not especially convincing, but the reported activity of barium as a promoter of NO_x is intriguing. If anything like the conjectured mechanism is correct, barium additives would be expected to have wider-ranging effects on the combustion process. Particularly, barium would be expected to be effective in reducing the emissions of all of the products of incomplete combustion. The properties of barium which are responsible for this conjectured catalytic activity are unknown, and no rationale can be suggested for finding other such catalysts, other than investigating additional alkaline-earth metals. Calcium and strontium have both been reported as having some smoke suppressing properties^(38, 39, 40, 41). The potential of such additives for reducing the entire range of products of incomplete combustion is such that additional investigations to resolve the matter may be warranted.

2. Approach of Adding an Active Oxidant Species

The second listed suggestion of introducing a "new" active oxidant does not appear attractive if it is considered as a homogeneous (gas phase) oxidant. Any oxygen-based specie would be expected to rapidly equilibrate to native species such as O or OH, and species based on other elements, e.g., fluorine, are likely to result in emissions potentially more objectionable than the products of incomplete combustion. In contrast, a specific class of heterogeneous (solid phase) oxidants, namely, oxidation catalysts, are known and applied in many situations.

The initial formation of a reactive fuel fragment or oxygen-containing radical in a homogeneous system has a large activation energy and, hence, occurs at a significant rate only at high temperatures. Oxidation catalysts achieve a similar result at much lower temperatures. This is accomplished by what can be crudely regarded as splitting the formation of an active specie into two or more reactions, having individually modest activation energies. Hence, while catalyzed combustion reactions at modest temperatures are much slower than the high-temperature reactions in flames, they are much faster than the homogeneous combustion process at the same modest temperature.

The difficulty in applying heterogeneous oxidation catalysts as additives to control emissions from combustion processes is that the combustible fuel molecules or particles must have physical contact with the catalyst. This can be arranged by passing the gas stream through a bed of catalyst, i.e., a catalytic afterburner. When the catalyst is used as a fuel additive, some care is required to insure that the additive in its functional form is well dispersed or, perhaps better, is concentrated in the region where its activity is needed. Otherwise, large quantities would be required, and most catalysts are relatively expensive and are potential pollutants themselves. At least in the case of fuel additives for liquid fuels, the initial dispersion can be obtained by using the additive in an oil soluble form.

In the literature reviewed in Part II of this report, there are suggestions that the effectiveness of smoke-suppressing, metal-based additives is related to the thermal stability of the particular compound used. The observed differences might also easily include an effect of volatility. It is not clear that the thermal stability and volatility of metal-bearing additives has been sufficiently investigated to assure that optimum effectiveness has been obtained.

The possibility that oxidation catalysts might reduce emission of coke particles seems not to have been investigated as such. The chemical form of the additive for greatest activity may well be different than that for smoke suppression.

Finally, if the catalytic additive has been dispersed as extremely fine particles, say through the vapor-phase oxidation or pyrolysis of a metal-containing organic, sufficient contact with gaseous pollutants may be achieved to produce noticeable reductions in "hydrocarbons", CO, and POM emissions. Thus, a reduction in CO emissions has been observed when using a manganese smoke suppressant⁽⁴²⁾. While this may not represent a practical approach to control of these gaseous pollutants, additional investigation might be justified.

3. Approach of Inhibiting Formation of Unreactive Combustible Material

Soot and POM are believed to be formed from some 2-carbon fragment, possibly derived from a precursor 1-carbon fragment. Thus, one might look for an additive that would stabilize or destroy these fragments. Destruction would be most likely accomplished by an oxidant, and this has been discussed previously. Stabilization, by some chain termination process may have merit, but the choice of an agent is not obvious. In view of the many species already available in flames which might cause termination, it is apparent that the reactive materials are either resistant to termination or easily reactivated after termination. Also, any agent likely to terminate the POM and early soot-building steps would likely react with other radicals in the flame, consuming the agent or leading to undesirable changes in the overall burning process. Nevertheless, currently available information does not preclude the possibility that some smoke-suppressant additives might function in this manner.

In the case of soot, it might be possible to interfere with the nucleation, growth, or agglomeration steps, even though the production of "soot molecules" was not prevented. If this can be done, the smaller particles or molecules may be destroyed in subsequent parts of the flame, or they may be emitted in less visible and possibly less objectionable forms. It is suspected that gaseous diluents and water sprays may function in this manner, either by the simple process of diluting the precursors and thus reducing the particle growth rate, by some unquantified thermal effect, or perhaps by some as yet unsuspected mechanism.

If the suggestion that electric charges and fields play an important role in the nucleation, growth, and agglomeration of soot is correct, then a rational basis for investigating potential additives can be suggested. If flame ions serve as nuclei for soot particle growth, then one could try to either reduce the ionization level, thus eliminating nuclei, or to greatly increase the ionization level, providing so many nuclei that no individual particle could grow to significant size. Also, if the ionization level in the flame is increased, electric fields would be reduced by the increased conductivity. The easily ionized alkali metals (and to a lesser extent the alkaline earth metals) are effective in increasing the ionization level in flames, whereas chlorine (and to a lesser extent hydrogen) are effective in suppressing ionization. The effects of alkali metals (introduced as nitrates and chlorides) on soot emissions have been reported to vary with the specific metal, the metal concentration, and the flame temperature.⁽⁴³⁾ Both promoting and inhibiting activity was observed. It should be possible to devise experimental additives that could either increase or decrease the flame ionization level and quite possibly control the position in the flame at which the additive became effective.

There would seem to be little that an additive could do to affect the formation of coke particles in a pulverized coal flame, but perhaps some effect might be obtainable with residual oil. If the pyrolysis reactions leading to coke formation proceed by a free-radical chain mechanism, then one might envision adding a free-radical scavenger to the oil in hopes of delaying the pyrolysis reactions and thus, hopefully, vaporizing a greater portion of the oil. Free-radical scavengers are in fact used as stabilizers and oxidation inhibitors in liquid oils at low temperatures. However, for coke inhibition, the agent would need to survive and be active at temperatures above 600 F. It is not immediately obvious that this is an impossible requirement, and perhaps such agents might be found.

An alternative approach might be to incorporate a cracking catalyst in the oil that would promote the formation of gaseous species with high carbon-hydrogen ratios, olefins, cyclics, aromatics, etc., rather than gaseous species with lower carbon-hydrogen ratios and coke. The requirements for such a catalyst, both physical and chemical, may be impossible to meet.

CONTROL OF EMISSIONS FROM FUEL IMPURITIES -- POSSIBLE OPPORTUNITIES FOR ADDITIVE ACTION

As indicated previously, additives cannot be expected to directly influence emission of elements that are present as impurities in the fuel. However, additives may influence the chemical or physical form of an impure element, either reducing or eliminating its objectionableness or facilitating its removal from the combustion gases. For example, sulfur has been added to low-sulfur coals to improve fly-ash collection in electrostatic precipitators⁽⁴⁴⁾, and iron scale and lime were occasionally added to coal to flux the ash and correct operating problems encountered by some boilers when firing coals with high ash-fusion temperatures. More recently, materials such as limestone and

dolomite have been used in residual-oil-fired boilers as Class III additives to reduce the SO_3 content of the flue gas and avoid fireside corrosion or acid-smut emissions. MgO has also been so employed and may function as either a reactant for the SO_3 or as an inert, non-catalytic coating on boiler surfaces.

There is little in the known mechanisms of pollutant formation from fuel impurities to suggest opportunities for additive action beyond that which has been demonstrated. Only one suggestion for a Class II additive can be made on the basis of chemical mechanism: To inhibit the reaction between SO_2 and O atoms and thus reduce the quantity of SO_3 generated. This could most likely be done by reducing the O atom concentration; such an action would be likely to have many adverse effects on combustion processes generally. A more useful suggestion (constituting a Class III additive approach) might be to search for an additive that would promote the reaction of SO_2 with chemical reactants such as lime, sodium carbonate, etc., and thus increase the efficiency of these reactants. As the mechanism by which these reactions occur is not known, no suggestions of logical candidate additives can be made.

For control of fly-ash particulate, there may be opportunity for an effective additive (other than sulfur) that would decrease the electrical resistivity of fly ash and thus promote its collection by electrostatic precipitators⁽⁴⁴⁾. Some combustion additives could conceivably have a corollary effect in reducing fly-ash resistivity, and an investigation of such possibilities may be warranted.

CONTROL OF NITROGEN OXIDES --
POSSIBLE OPPORTUNITIES FOR ADDITIVE ACTION

In terms of the objectives of this study, namely the identification of approaches by which pollutant emissions may be controlled with additives, the prospects for NO emissions are very poor. As stated earlier, one can effect large reductions in NO by combustion modification procedures.

For example, two-stage combustion operates through a rich initial zone and then a lean-burning zone. In effect, the temperature of the combustion process is reduced in the rich zone and unburned hydrocarbon and CO are oxidized, again at lower temperature, in the second, lean, zone. It appears that this two-stage procedure can be moderately effective in reducing NO emissions from chemically-bound-nitrogen fuel systems also. In this instance, the organic nitrogen compound in the first, fuel-rich, stage of combustion will break down via a pyrolysis path as well as via an oxidation path. Depending on the relative effectiveness of these two paths (i.e., the quantity of organic nitrogen going to nitrogen $RN \rightarrow N_2$) two-stage combustion can be effective in reducing NO⁽⁴⁵⁾

The control of NO with additives requires that the additive operate on the Zeldovich mechanism to reduce thermal fixation reactions or on the chemically-bound nitrogen to reduce or divert organic-nitrogen oxidation processes. To affect either of these processes requires that an additive

1. promote the recombination of O- and/or N-atoms,
2. retard the production of O- and/or N-atoms,
3. promote the pyrolysis of organic-nitrogen compounds, or
4. promote the reduction of NO.

Each of these approaches to NO_x control is discussed below.

1. Promotion of Atom Recombination

A variety of gaseous species can promote the recombination of O-atoms, i.e., SO_2 , H_2O ; but generally, these species cannot promote the recombination at a sufficiently significant level to noticeably reduce NO. Heterogeneous catalysts may also be effective as third-body surface for atom recombination, but here too, one would require a large concentration of additive to affect the reduction, which in turn might act to the detriment of the total combustion process.

2. Retardation of O-Atom Production

Materials such as halogen compounds and the cyclopentadienyl compounds are known flame retardants. It is quite possible that, acting in this capacity, these inhibitors can also effect a reduction in NO emission by interfering with the hydrocarbon oxidation process and reducing the level of O-atoms. Although there is evidence that the addition of a number of organo-metallic compounds has resulted in reduced NO, the additive was added in most instances for other purposes (to reduce particulate) and the effect on NO was only of secondary concern. In most cases, it appears that these additives were selected by chance more than by design. A more concentrated effort might be warranted, therefore, to understand the role of the additive in these instances.

3. Promotion of Pyrolysis Reactions

An additive which might promote the pyrolysis of organic-nitrogen compounds could be useful in reducing NO in organic-nitrogen fuel systems. Halogens and oxygen can catalyze the pyrolysis of organic species; whether or not such species can catalyze organic-nitrogen compounds and whether they can direct the decomposition toward N_2 is not known. It is also recognized that different organic-nitrogen compounds pyrolyze by different reaction paths. For example, CN-bonded compounds (i.e., cyanogen) yield much less NO than NH-bonded compounds. Why these compounds behave as they do is not known. One might, therefore, examine this problem in more detail

to determine whether specific additives might be applied for the purpose of directing the decomposition process.

4. Reduction of NO

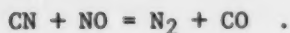
There is sound evidence that NO can be reduced in flame processes. As discussed earlier, NO yields in organic-nitrogen flame systems

1. decrease as the concentration of organic nitrogen is increased, and
2. decrease as the fuel/air ratio is increased.

This reduction appears to be related to reactions of the type



where X may be a nitrogen-containing radical or an organic radical. It follows then that ammonia, CO, or hydrocarbons might be employed as "additives" to reduce NO. Obviously, if these species are added to the fuel, the effect will be similar to the combustion of organic nitrogen or hydrocarbon under richer conditions. On the other hand, it is also conceivable that these N- or organic species can be added to the postflame gases to reduce NO^(6, 19). In this capacity, one is seeking additives that will yield high concentrations of N, NH_x, CN, or CH_x radicals which will attack NO by the following types of reactions:



Exxon's patent⁽⁴⁶⁾ on ammonia addition under controlled temperature conditions apparently operates via the reaction scheme,



KVB⁽⁴⁸⁾ has also shown ammonia additions to be very effective, reducing NO by some 90 percent when injected at temperatures of 1300 - 2000 °F to the combustion gases in a combustion tunnel. In a sense, these procedures may be referred to under Class III "Additive Control" (See Table 1), however, the reduction of NO is carried out so close to the region of NO formation it is warranted to be considered in this discussion. In a similar manner Wendt, Sternling and Matovich⁽⁴⁷⁾ have shown reduction of SO₃ by additions of CO or methane, and reductions of NO by additions of ammonia or methane downstream of the flame zone.

The chemistry and kinetics of these processes have not been explored in detail yet. They have to be considered as speculative processes, although the evidence to date does suggest that such processes are occurring. Whether and/or to what extent additives can be employed properly to affect the conversion of NO to N₂ is speculative.

In summary, several approaches are presented here which must be viewed with some reservation. It is not inconceivable that additives might be employed to control NO in combustion processes; however, it is highly speculative that additives can be employed practically to effect substantial reductions of NO in full-scale combustion systems.

* * * * *

Experimental investigations of combustion-type fuel additives are reviewed in Part II which follows.

PART II

REVIEW OF EXPERIMENTAL INVESTIGATIONS OF COMBUSTION-TYPE FUEL ADDITIVES

SCOPE OF REVIEW

A compilation of the additives for petroleum fuels, with a discussion of their uses and mechanisms of action, was published 12 years ago by Lodwick⁽¹⁵⁾. More recently, Finfer⁽⁴⁹⁾, Agius et al⁽¹⁰⁾, and Salooja⁽⁵⁰⁾ published reviews of fuel-oil additives that were directed primarily at soot and smoke emissions. Salooja also considered corrosion inhibitors in his review. Pertinent data from these publications have been combined in this review with more recent information to determine the state of the art for additives that have been investigated for their effects on one or more air pollutants. Results of experiments conducted as part of the current EPA program are to be covered in detail in a separate report⁽³⁾.

In this review, emphasis was placed on identification of technical literature in which quantitative measurements on additive effectiveness are reported. Effects of specific chemical compounds were of interest; proprietary additives have not been considered unless the compounds that are major components of the additive are known. Some data have been included from studies in which only the metal component of the additive was designated, provided the data were particularly pertinent to the discussion.

Most of the additive studies reported in the literature were carried out in the laboratory under controlled conditions, but there are also a significant number of full-scale boiler tests, mostly with oil firing. Sulfur trioxide received the greatest attention in past years because it was chiefly responsible for the corrosion and deposit problems. Recently, attention has been directed to particulate, nitrogen oxides, and polycyclic organic materials.

Summary Tables

Tables 2, 3, and 4 summarize the quantitative data found in the technical literature for combustion additives, grouped according to chemical type of the additive:

Table 2. Effects of Organometallic Additives on Combustion Emissions (2 pages)

Table 3. Effects of Inorganic Additives on Combustion Emissions

Table 4. Effects of Organic Additives on Combustion Emissions.

For each additive or chemical compound, the following information is listed under the applicable pollutant: fuel type, additive concentration, pollutant reduction, and reference number. Additive concentrations generally have been converted to volume percent or weight percent (or are in the units originally reported). Data on pollutant effects have been expressed for this review as "percent reduction" for each pollutant affected; thus, "0" denotes that the additives showed no effect on the pollutant in question.

Most of the data in the tables are based on experiments with boilers or laboratory simulations of boiler or furnace firing. Observations applying to gas turbines and IC engines are noted in the tables.

TABLE 2. EFFECTS OF ORGANOMETALLIC ADDITIVE COMPOUNDS ON COMBUSTION EMISSIONS

ADDITIVE	PARTICULATES			POLYCYCLIC ORGANIC MATTER (as BaP or Total PAH)			SULFUR TRIOXIDE (unless SO ₂ indicated)			NITROGEN OXIDES		
	Fuel Type	Additive conc	Reduction, percent	Ref.	Fuel Type	Additive conc	Reduction, percent	Ref.	Fuel Type	Additive conc	Reduction, percent	Ref.
Naphthenates	No. 2	0.003 w/o metal	70	38	-	-	-	-	No. 2	0.5 v/o	10	89
	-	-	-	-	-	-	-	-	-	1.0 v/o	15	89
	No. 2	0.01 w/o	15	53	-	-	-	-	J-A ^a	0.2 w/o metal	25	101
Manganese	-	-	-	-	-	-	-	-	-	0.5 w/o metal	30	101
	No. 2	0.003 w/o metal	65	38	-	-	-	-	No. 2	0.5 v/o	10	89
	-	-	-	-	-	-	-	-	-	1.0 v/o	10	89
Iron	No. 2	0.02 w/o	17	53	-	-	-	-	J-A ^a	0.2 w/o metal	20	101
	-	-	-	-	-	-	-	-	-	0.5 w/o metal	30	101
	No. 2	0.01 w/o	50	54	-	-	-	-	No. 2	0.5 v/o	6	89
Lead	No. 2	0.003 w/o metal	30	38	-	-	-	-	-	1.0 v/o	9	89
	-	-	-	-	-	-	-	-	-	-	-	-
	No. 2	0.01 w/o	10	53	-	-	-	-	-	-	-	-
Zinc	-	-0.05 w/o	22	53	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Nickel	No. 2	0.02 w/o	25	53	-	-	-	-	No. 6	0.2 w/o	100	77
	-	-	-	-	-	-	-	-	-	0.07 w/o	75	78
	-	-	-	-	-	-	-	-	-	0.14 w/o	100	78
Magnesium	No. 2	0.02 w/o	7	53	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
	No. 2	0.01 w/o	10	53	-	-	-	-	No. 6	0.15 w/o	100	77
Copper	-	-	-	-	-	-	-	-	-	-	-	-
	No. 2	0.01 w/o	10	53	-	-	-	-	No. 6	0.07 w/o	100	80
	-	-	-	-	-	-	-	-	-	-	-	-
Ferrocene	No. 6	0.003 w/o	37	52	-	-	-	-	J-A ^a	0.2 w/o metal	16	101
	-	-	-	-	-	-	-	-	-	0.5 w/o metal	18	101
	No. 2	0.012 w/o	47	1	-	-	-	-	No. 6	0.003 w/o	0	52
No. 2 ^a	-	0.1 w/o	45	60	-	-	-	-	No. 2	0.012 w/o	0	1
	-	0.2 w/o	82	60	-	-	-	-	-	-	-	-
	No. 2	0.01 w/o	28	53	-	-	-	-	-	-	-	-
PC	-	0.05 w/o	45	53	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
	PC	0.001 w/o	NS	71	-	-	-	-	-	-	-	-
P-A	-	1.5 ⁺⁺⁺	28	57	-	-	-	-	-	-	-	-
	-	2.5 ⁺⁺⁺	30	57	-	-	-	-	-	-	-	-

Boiler, furnace or continuous-combustion laboratory apparatus, unless noted by asterisk (*) or ex.

* Experiments conducted on gas-turbine combustor.

** Experiments conducted on reciprocating IC engine (for simulation bench).

Fuel

No. 2 or No. 6 Fuel Oil
PC -- Pulverized Coal
BC -- Bituminous Coal
SC -- Steamer Coal
CC -- Coal Gas
J-A -- Jet A liquid fuel
P-A -- kerosene + Acetylene
(concentrations are in
8 metal/vapour)

Additive Concentration

v/o -- volume percent
w/o -- weight percent
NS -- not specified

Pollutant

BaP -- Benzo(a)pyrene
PAH -- Polynuclear aromatic
hydrocarbons

TABLE 2. EFFECTS OF ORGANOMETALLIC ADDITIVE COMPOUNDS ON COMBUSTION EMISSIONS (Continued)

ADDITIVE	PARTICULATES			POLYCYCLIC ORGANIC MATTER (as BAP or Total PAH)			SULFUR TRIOXIDE (unless SO ₂ indicated)			NITROGEN OXIDES		
	Fuel Type	Additive conc.	Reduction, percent	Ref.	Fuel Type	Additive conc.	Reduction, percent	Ref.	Fuel Type	Additive conc.	Reduction, percent	Ref.
Iron carbonyl	No. 6	0.003 w/o	40	52	P-46	1.5***	32	57	No. 6	0.003 w/o	0	52
	P-46	1.5***	32	57		2.5***	50	57				
C ₅ H ₅ -Ni-(CO) ₃	No. 2**	0.1 w/o	14	60								
	PC	0.2 w/o	18	60								
	PC	0.1 w/o	88	71								
CH ₃ SiMe ₃ -Ni-(CO) ₃	P-46	1.5***	80	57	P-46	1.5***	81	57				
		2.5***	82	57		2.5***	97	57				
	No. 2	0.012 w/o	80	38					No. 2	0.01 w/o	0	1
Tetraethyl lead	No. 2	0.01 w/o	44	1					No. 6	100	45	80
	No. 2	0.01 w/o	5	53								
	No. 2	0.05 w/o	20	53								
Calcium sulfonate	No. 2	0.03 w/o	45	38								
Sodium sulfonate	No. 2	0.2 w/o	66	63								
Copper sulfonate	No. 2	0.01 w/o	50	54								
Diethyl phosphates	No. 2	0.26 w/o	28	39								
Me + Zn ethyl benzenes	No. 2**	0.6 w/o	85	59								
Nickel carbonyl	No. 2	0.009 w/o	40	38								
Chromium carbonyl	No. 2	0.013 w/o	60	38								
Ni veracetate	No. 2**	1 w/o	10	64								
Co veracetate	No. 2**	1 w/o	10	64	Gasoline**	1 w/o	66	64				
Er molybdate												
Copper chelate	No. 2	0.0075 w/o metal	50	66								
		0.001 w/o metal	50	66								
Oil-sol B Compound	No. 2**	0.05 w/o	49	83								
		0.18 w/o	80	65								

Boiler, furnace or continuous-combustion laboratory apparatus, unless noted; b) asterisk (*) or **

* Experiments conducted on gas-turbine combustor.

** Experiments conducted on reciprocating IC engine (or simulation bomb).

Exhaust

No. 2 or No. 6 Fuel Oil
PC -- Pulverized Coal
EC -- Bituminous Coal
SC -- Subbituminous Coal
CC -- Coal Gas
P-46 -- Jet A liquid fuel
*** Pentane + acetylene (concentrations are in 8 metal/vapor)

Fuel

Mixture Concentration
v/o -- volume percent
w/o -- weight percent
NS -- not specified

Fallstent
BAP -- Benzoin pyrene
PAB -- Polynuclear aromatic hydrocarbons

TABLE 3. EFFECTS OF INORGANIC ADDITIVE COMPOUNDS ON COMBUSTION EMISSIONS

ADDITIVE	PARTICULATES			POLYCYCLIC ORGANIC MATTER (as 2AP or Total PAH)			SULFUR TRIOXIDE (unless SO ₂ indicated)			NITROGEN OXIDES		
	Fuel Type	Additive conc.	Reduction, percent	Fuel Type	Additive conc.	Reduction, percent	Fuel Type	Additive conc.	Reduction, percent	Fuel Type	Additive conc.	Reduction, percent
Mg metal	-	-	-	-	-	-	No. 6	85	60-75	-	-	-
MgO	-	-	-	-	-	-	No. 6	0.02 w/o	100	-	-	-
MgO + Al ₂ O ₃	No. 6	0.05 w/o	6	-	-	-	No. 6	0.35 w/o	100	-	-	-
MgCO ₃	-	-	-	-	-	-	No. 6	0.05 w/o	100	-	-	-
CeO	-	-	-	-	-	-	No. 6	0.05-0.1 w/o	75	-	-	-
Bismuthite	-	-	-	-	-	-	PC	NS	50	-	-	-
	-	-	-	-	-	-	No. 6	1 w/o	99	-	-	-
	-	-	-	-	-	-	No. 6	0.8 w/o	100	-	-	-
	-	-	-	-	-	-	No. 6	0.1 w/o	47	-	-	-
	-	-	-	-	-	-	No. 6	0.2 w/o	50	-	-	-
	-	-	-	-	-	-	No. 6	0.15-0.2 w/o	80	-	-	-
Ce(NO ₃) ₂	Propane	0.2 w/o	72	-	-	-	BC	0.375 w/o	50	-	-	-
CeCl ₂	-	0.1 w/o	25	-	-	-	-	-	-	-	-	-
Zn Metal	-	-	-	-	-	-	-	-	-	-	-	-
ZnO	-	-	-	-	-	-	-	-	-	-	-	-
NaOH	-	-	-	-	-	-	No. 6	0.45 w/o	100	-	-	-
Na ₂ CO ₃	-	-	-	-	-	-	SC	0.25 w/o	100	-	-	-
NaHCO ₃	-	-	-	-	-	-	CC	0.0045 g/l	85	-	-	-
	-	-	-	-	-	-	PC	NS	47(SO ₂)	-	-	-
Ba(NO ₃) ₂	-	-	-	-	-	-	No. 6	3.3 w/o	36(SO ₂)	-	-	-
SeCl ₂	Propane	0.042 w/o	60	-	-	-	SC	14 w/o	70(SO ₂)	-	-	-
MnO ₂	Propane	0.07% w/o	56	-	-	-	-	3.4 w/o	23(SO ₂)	-	-	-
	No. 6	0.006 w/o	15	-	-	-	-	-	-	-	-	-
Pitch	-	0.007 w/o	77	-	-	-	-	-	-	-	-	-
SiO	-	-	-	-	-	-	No. 6	0.006 w/o	0	-	-	-
SiO ₂	-	-	-	-	-	-	CC	2 g/cu ft	80	-	-	-
	-	-	-	-	-	-	No. 6	0.45 w/o	50	-	-	-

Insoluble

Boiler, furnace or continuous-combustion laboratory apparatus, unless noted by asterisk (*) or so).

* Experiments conducted on gas-turbine combustor.

so Experiments conducted on reciprocating IC engine (or simulation bomb).

Fuel

No. 2 or No. 6 Fuel Oil

PC -- Pulverized Coal

BC -- Bituminous Coal

SC -- Stoker Coal

CC -- Coal Gas

J-A -- Jet A liquid fuel

P-W -- Pentane + Acetylene

sox (concentrations are in g metal/l; vapor)

Additive Concentration

w/o -- volume percent

w/o -- weight percent

NS -- not specified

Pollutants

Ref -- Benzolepyrene

PAH -- Polynuclear aromatic hydrocarbons

Organization of Part II Review Discussion

In the report sections which follow, experimental data and some qualitative comments on additives reported in the literature are discussed according to observed effects of combustion-type fuel additives on emissions of the four pollutant classes:

- Particulate and Smoke
- Polycyclic Organic Matter (POM)*
- Sulfur Oxides
- Nitrogen Oxides.

Separate sections covering effects on these pollutants follow.

ADDITIVE EFFECTS ON PARTICULATE EMISSIONS AND SMOKE

Many of the fuel-additive investigations reported in the literature have been directed at reduction of particulate emissions. The attention has centered primarily on fuel-oil combustion, because it has been demonstrated that additives can be of value in this area. For coal-fired systems, most of the fuel additive work has been designed to reduce corrosion and deposits, and any effect on particulate emissions has been observed only as incidental to these other objectives.

COMBUSTION ADDITIVES IN FUEL-OIL

The interest in reducing smoke from residential or commercial heating units, from gas turbines and from vehicles powered by diesel engines has provided impetus for much of the study of additives. Consequently, much of the work has been done with distillate fuels, with only occasional investigation of heavier oils.

* POM emissions are frequently reported in the literature as benzo[a]pyrene (BaP) determinations, or as polynuclear aromatic hydrocarbons (PAH) as a class. These are the terms used in Tables 2, 3, and 4.

Investigations Firing Residual Oil in Boilers

In the course of their study of residual oil additives in low-pressure heating boilers, Lee and his associates⁽⁵¹⁾ included measurements of particulate emissions. In a research boiler fueled with No. 6 oil, they found only a slight reduction in particulates when using a hydrated magnesium oxide-aluminum oxide mixture as an additive. This additive was designed to control SO_3 and consequent sulfuric acid corrosion, and it was found to bring about only a 6 percent reduction in particulates when added to the oil in concentrations of 0.05 to 0.1 volume percent.

On the other hand, work at the New England Power Company was aimed at reducing particulate emissions from an oil-fired power station.⁽⁵²⁾ These tests were carried out in a 250 megawatt unit at the Brayton Point Station just after it was put in service following the annual maintenance shutdown, so that the additive performance was evaluated in a clean boiler. A 40-percent reduction in particulate emissions was obtained with an addition of 8 ppm of iron in the form of iron carbonyl. The same amount of iron added as ferrocene resulted in 37 percent reduction in particulates. Another additive tested was an inorganic formulation containing manganese dioxide, but this additive provided only a 15 percent reduction in particulates although it was used at a concentration of 25 ppm manganese in the oil. It also was noted in this study that the amount of particulate reduction at a constant additive level was a function of the oil viscosity as well, and in the case of the iron carbonyl additive, the particulate loading went through a minimum at a viscosity of 100 SSU and increased substantially at higher viscosities of the oil. (This may be due to the fact that the carbon particulate emission level is influenced by oil viscosity as fired.)

Investigations Firing Distillate Oil
in Furnaces, Boilers, and Gas Turbines

Martin, Pershing, and Berkau⁽¹⁾ studied the effect of some 200 different materials as additives to No. 2 fuel oil in the EPA experimental furnace with a conventional high-pressure atomizing, gun-type burner. Fewer than 10 percent of the fuel additives produced any pollutant reduction; in a few cases, proprietary organo-metallic additives substantially reduced particulate emissions.

In this work, ferrocene was used at a concentration of 0.012 weight percent and a particulate reduction of 47 percent was observed. The methyl derivative of cyclopentadienyl manganese tricarbonyl also was investigated in this study, and a particulate reduction of 44 percent was observed at an additive concentration of 0.01 weight percent. It is very significant that Martin et al found that when additive concentrations were greater than 0.01 weight percent, the amount of particulate began to increase as a result of the increasing concentration of additive metal.

The authors raise the question about possible toxicity of the resulting metallic emissions. They conclude that the use of burner designs having improved air/fuel mixing can achieve greater carbon particulate reduction and is recommended over the use of distillate fuel additives for residential heating applications.

The greatest reduction in particulates when firing No. 2 oil in a domestic heater unit was reported by Riggs and his colleagues⁽³⁸⁾. The addition of methyl cyclopentadienyl manganese tricarbonyl at a rate of 0.1 gram of metal per gallon of fuel resulted in an 80 percent reduction in particulates. Cobalt and manganese naphthenates were only slightly less effective, providing reductions of 70 percent and 65 percent respectively at the same concentration in the oil. Chromium carbonyl was the next most effective with 60 percent reduction in

particulates. The three other compounds studied were less effective, the percent reduction being: calcium sulfonate, 45 percent; nickel carbonyl, 40 percent; and lead naphthenate, 30 percent.

Weeks and his associates⁽⁵³⁾ used a conventional gun-type oil burner firing No. 2 oil in a typical domestic steam boiler for their additive study. Ferrocene was the most effective additive that they found, with particulate reductions ranging from 28 to 45 percent as the additive concentration increased from 100 to 500 ppm. The other additives that they studied did not reduce the particulates nearly as effectively as did the ferrocene. The percent reductions in particulates obtained with the various naphthenates were as follows: nickel, 25; iron, 22; manganese, 17; cobalt, 15; copper, 10; and magnesium, 7. Tetraethyl lead also was used in a concentration of 500 ppm and provided a particulate reduction of 20 percent.

Organometallic additives also were investigated by Vaerman⁽⁵⁴⁾ who worked with a domestic steam boiler burning No. 2 oil. At a concentration of 0.01 weight percent, both manganese naphthenate and copper sulfonate reduced the particulate emissions by 50 percent. Vaerman also noted that the efficiency of the additive was a function of the CO₂ content of the combustion gases as well; he concluded that particulate emissions for domestic units could be kept within acceptable limits by burner adjustment, and additives would not be necessary.

Full-scale tests on power-station gas turbines fueled with No. 2 oil were conducted by Plonsker and his colleagues,⁽⁵⁵⁾ using methyl cyclopentadienyl manganese tricarbonyl additive. Turbines at three utilities were included in this program, and reductions in smoke, particulates, and carbon emissions ranged from 50 to 90 percent at manganese concentrations of 20 to 100 ppm. In general, the greatest emission reductions were observed at higher turbine load conditions and higher manganese concentrations.

Organometallic compounds of barium, manganese, iron, lead, and boron were tested by Shayeson⁽⁵⁶⁾ in JP-5 jet fuel. The Ba, Mn, and Fe compounds eliminated smoke in laboratory tests at concentrations of 0.5 volume percent, 0.08 volume percent, and 0.05 weight percent, respectively. Lead and boron compounds were ineffective. At lower concentrations, Mn was most effective. At 0.04 volume percent, the Mn compound eliminated smoke in a full-scale engine test. However, in a flight test, as much as 0.1 volume percent would not completely prevent smoke formation.

Laboratory Scale Investigations Firing Various Fuels in Continuous Combustion Apparatus

In a series of experiments with diffusion flames in which mixtures of pentane and acetylene were burned, Spengler and Haupt⁽⁵⁷⁾ found that methyl cyclopentadienyl manganese tricarbonyl was very effective in reducing the amount of particulate formed, although the additive was used at a relatively high concentration. Eighty percent reduction in particulates was achieved with an additive concentration containing 1.5 grams of metal per liter of combustible vapor. Ferrocene and iron carbonyl were only about half as effective at the same metal concentration.

The effects of 40 metals on the amount of soot emitted by a laboratory-scale propane diffusion flame were investigated by Cotton et al⁽⁴⁰⁾. The metals were added to the flames by atomizing aqueous solutions of their salts into the fuel with a stream of nitrogen. The most effective compound found in their work was barium nitrate, with which a 60 percent reduction in soot occurred with enough additive to provide a carbon-to-barium ratio of 3700. Calcium nitrate and strontium chloride were found to be slightly less effective. Some soot reduction also was obtained with ammonium molybdate and sodium tungstate, but all the other metals tried were ineffective. The authors concluded that in

terms of the metal concentrations required and the equivalence ratio at which the additive was effective, only the three alkaline earth metals could be considered as promising additives.

Cotton et al⁽⁴⁰⁾ hypothesize from this study that metal additives reduce carbon emission by two basic mechanisms (a) the alkaline earth metals, and probably molybdenum, catalyze the production of free radicals via the decomposition of hydrogen or water, and (b) other metals probably catalyze the oxidation of soot in cooler parts of the flame after being incorporated with the soot particle.

Friswell's⁽³⁷⁾ later studies in a rig simulating a gas-turbine combustor with Ba and Mn additives in jet fuel tend to support these hypotheses. Support for the radical production mechanism is also found in the observation that NO production was increased at the same time that Ba addition reduced soot formation. Mn, and also Fe, appeared to operate by catalyzing the burn-out of the soot. In accord with these hypotheses, Mn and Fe operated better as the air/fuel ratio approached the stoichiometric level.

Alkali metals were investigated by Feugier⁽⁴³⁾ for their effectiveness in reducing soot formation in ethylene flames. Nitrate and chloride salts of the metals were volatilized and carried into the flame in a stream of nitrogen. At the highest flame temperatures lithium reduced the soot formation while cesium, potassium, and sodium increased it. As flame temperatures were lowered, these three metals gave small reductions in emissions at low metal concentrations, but not at high concentrations.

Investigations Firing Distillate Oil in I.C. Engines

In their work on polycyclic aromatic hydrocarbons, Ray and Long⁽⁵⁹⁾ also measured the effect of additives on the particulate formation in diesel engines. They employed fairly large amounts of the additives, and observed a 57 percent reduction in particulates when tertiary-butyl hydroperoxide was added at a rate of 0.5 volume percent. They found that 1-nitropropane gave only a 34 percent reduction in particulates when applied at 5 volume percent. It also was noted in this series of experiments with additives that the amount of carbon residue remaining in the engine remained constant even through the particulate matter emitted from the system was reduced by the additives. On this basis, the author suggested that different reaction mechanisms are responsible for the formation of particulates and of the carbonaceous residue remaining in the engine.

A recent patent by Cities Services Oil Company⁽⁵⁹⁾ claimed a very significant reduction in particulate emissions from distillate fuel burned in a diesel engine. In this case, a solution of barium and zinc 2-ethyl-hexanoates (10 to 1 barium to zinc by weight) with methyl cellosolve in a hydrocarbon reduced the smoke number reading by an amount equivalent to a reduction of about 85 percent in the particulate emission. (Particulate loading is not a linear function of smoke number.)

Experiments conducted in a constant-volume bomb which simulated the conditions obtained in a diesel engine were reported by Chittawadgi and Volnov⁽⁶⁰⁾. When ferrocene was added to the fuel in a concentration of 0.2 weight percent, particulates were reduced about 80 percent. The smoke reduction dropped to about 45 percent when the ferrocene concentration was cut in half. These investigators also tried cyclopentadienyl manganese tricarbonyl as an additive but obtained only 18 percent reduction in particulates at an additive level of 0.2 weight percent.

Other organic additives are reported to have been effective in reducing particulate emissions in the combustion of No. 2 oil in a diesel engine. Churchill and Mitchell⁽⁶¹⁾ reported that 0.05 weight percent of hydrazine gave a 50 percent reduction; a patent granted to the Cities Service Oil Company⁽⁶²⁾ also claimed 50 percent smoke reduction by the use of dialkylethers of ethylene glycol when No. 2 oil was burned in a single cylinder diesel engine.

Salts of organic acids have been used for smoke reduction. Barium sulfonate⁽⁶³⁾, the barium and strontium salts of dialkyl ortho phosphoric acids⁽³⁹⁾, and the manganese and cobalt salts of versatic acids⁽⁶⁴⁾ have all been used with some measure of success.

Additional Investigations

There are some additional reports in the literature of effective performance by fuel additive compounds which are not completely characterized. The oil-soluble barium compound used by Golothan⁽⁶⁵⁾, which was mentioned earlier, reduced the particulate in diesel engine exhausts by 80 percent when used at a concentration of 0.18 weight percent. Amick and Hunt⁽⁶⁶⁾ formed a copper chelate by reacting cupric acetate with a mixture of paraformaldehyde, dodecylphenol, and ethylenediamine; when this chelate was added to distillate oil at a concentration of only 0.001 weight percent copper, a 50 percent reduction in particulate was obtained. Summaries of various additive field trials by Kukin^(67, 68) have claimed substantial reductions of particulate emission by using a proprietary formulation that is primarily an organo-manganese compound, either alone or in conjunction with MgO.

Survey Conclusions Related to Use of
Combustion Additives for Reducing
Particulate or Smoke Emissions From
Fuel-Oil Firing

Experimental evidence thus indicates that additives can be effective in lowering the carbonaceous portion of particulate emissions. They are particularly useful in oil-fired systems, because carbon constitutes a large percentage of the particulate emission. Oil-soluble compounds of certain transition metals (manganese, iron, nickel, and cobalt) or certain alkaline-earth metals (barium and calcium) have proven to be the most effective additives for reducing particulate emissions.

COMBUSTION ADDITIVES IN COAL FIRING

Very little effort has been devoted to the use of additives for the reduction of particulate formation in the combustion of coal. In past years, electrostatic precipitators or mechanical collectors have been used on large coal-fired equipment to reduce particulate emissions. (Many smaller coal-fired units have had no collectors.) From an ambient air-quality standpoint, further reductions in particulate emissions from coal firing are desirable.

The relatively large inorganic content of coal results in a certain irreducible minimum value of the particulate that will be formed. It is only the carbonaceous part of the particulate that will be reduced by the action of combustion fuel additives. Thus, it may not be economical to consider additives for such a purpose, unless a marginally-operating boiler that generates particulate emissions slightly exceeding regulatory limits can be brought into compliance by a small reduction in particulate. Also, the reduced carbon loss of the boiler could be advantageous to overall efficiency.

Only a few investigations of coal additives were identified in the survey, as noted below.

Early Investigations on Coal Additives
by the U.S. Bureau of Mines

One of the earliest investigations of the effectiveness of additives was made at the U.S. Bureau of Mines by Nicholls et al⁽⁶⁹⁾, to determine whether there was any merit in intermittent use of soot removers in coal-fired residential furnaces to keep heat transfer surfaces and stacks clean. Soot deposits from bituminous coal were treated with additives in a laboratory furnace to determine the ignition temperature of the soot^{*}; those materials that performed best were then compared in coal-burning home furnaces with fixed fuel beds. The results showed that of the many inorganic compounds used, copper compounds were the most effective in lowering the ignition temperature of soot and thereby promoting its combustion. The metal chlorides tried were ranked in decreasing order of effectiveness: CuCl_2 , PbCl_2 , NiCl_2 , SnCl_2 , NH_4Cl , KCl , FeCl_3 , MnCl_2 , ZnCl_2 , $\text{Ca}(\text{OCl})_2$, CaCl_2 , and NaCl . It was found that the benefits of CuCl_2 addition also could be obtained by using a 50-50 mixture of NaCl and CuSO_4 . No measurements were made of stack particulate emission.

Later, a broad experimental program was carried out over a 2-year period at the Bureau of Mines under the direction of Nicholls⁽⁷⁰⁾ to investigate the effects of inorganic compounds on the combustion of coal and coke. Twenty-five compounds mixed with coal were included in the study; and NaCl , CaCl_2 , and Na_2CO_3 received the most attention. Eleven coals and four cokes were used as fuels. The fuels were burned

* It should be noted that such additives that function downstream of the flame are not "combustion-type" fuel additives and are properly categorized as Class III additives.

in fixed beds carefully controlled laboratory conditions, and both underfeed and overfeed firing were investigated. The experiments showed that:

1. No increase in the burning rate of coal was obtained with any of the additives. Coke burned more rapidly with Na_2CO_3 addition.
2. None of the additives decreased the maximum density of smoke at the stack or the total quantity of smoke as indicated by a photometer in a stack section. In fact, the average tendency was for a slight increase in smoke when the additives were used.
3. The soot removal properties of CuCl_2 , PbCl_2 , and other chlorides were confirmed.
4. Formation of objectionable clinker was increased by most additives.

While these studies showed that additives could be effective in soot burnout to maintain clean flue passages and stacks, coal additives were not found effective in reducing particulate or smoke from fixed-bed coal firing.

Other Investigations on Coal Additives

A reduction in particulate emission was noted in a coal-fired power plant by Doxey and associates⁽⁴¹⁾ when they added calcium chloride to coal in order to prevent freezing. The emissions from a pulverized coal system equipped with an electrostatic precipitator were reduced 20 to 30 percent by the addition of 0.1 weight percent calcium chloride to the coal. This effect may be the result of lowered resistivity of the particulate material, thus enhancing precipitator performance. (In modern utility boilers, chlorides would not be added because of problems with external corrosion.)

Reduction of particulates in pulverized coal firing also was claimed by Kerley⁽⁷¹⁾ who added from 0.001 to 5.0 weight percent of ferrocene or cyclopentadienyl manganese tricarbonyl to the coal during the grinding process. The extent to which the particulates were reduced was not specified.

There is little likelihood of combustion-type fuel additives making significant reductions in particulate emissions from large pulverized coal burning equipment which normally emits only small quantities of carbon particulate and which in any event is usually equipped with electrostatic precipitators. In some circumstances, additives may be useful in enhancing the performance of the precipitators through decreasing the particulate resistivity, but these are generally added at the precipitator inlet and are considered Class III additives.

Survey Conclusions Related to Use of Combustion
Additives for Reducing Particulate Emissions
From Coal Firing

For large pulverized coal-fired equipment, fuel additives appear to hold little promise for directly reducing particulate or smoke emissions.

In smaller coal-fired equipment where the carbon content of the particulate emissions is high and mechanical collectors may be used rather than electrostatic precipitators, the potential of additives for reducing carbon particulate emissions may be greater. This could be particularly true for stoker firing, where much of the ash is retained in the furnace.

ADDITIVE EFFECTS ON POLYCYCLIC ORGANIC MATTER

A class of hazardous pollutants identified as polycyclic organic matter (POM) was defined in 1972 by the National Academy of Sciences⁽⁴⁾. The terminology, POM, now is coming into wider use. Broadly, this class of pollutant compounds includes (1) polynuclear aromatic hydrocarbons, commonly referred to in the literature as PNA or PAH, and (2) nitrogen-containing heterocyclic compounds.

Although POM is usually found in the atmosphere only in trace concentrations, it is of concern because of the highly carcinogenic nature of some of its compounds. The National Academy of Sciences has rated many of the individual compounds according to their currently known carcinogenicity⁽⁴⁾. Benzo[a]pyrene (BaP), one of the highly carcinogenic compounds, is sometimes used as a measure of total PAH or POM. Generally, POM emissions are the result of incomplete combustion and, thus, depend on combustion conditions. Hangebrauck and his associates⁽¹¹⁾ have characterized POM emissions from a variety of fossil-fuel combustion systems but did not investigate fuel additives.

Experimental investigations aimed at the reduction in POM emissions from combustion processes by additives have claimed significant results. Much of this work has been on gas flames and on diesel engines burning distillate oil, and it is questionable as to how much of the results are applicable to combustion of heavy oils or coal. No investigations were identified where additive effects on POM emission were reported for residual oil or coal firing. There is the additional question as to the adequacy of sampling and analytical techniques, inasmuch as techniques in these areas have advanced considerably in the past few years.

Laboratory Investigations in Continuous Combustion Apparatus

Significant work has been reported by Ray and Long⁽⁵⁸⁾ who studied the effects of several additives on the production of PAH in propane diffusion flames and a diesel engine. Dichloromethane as an additive increased the formation of soot and carbonaceous residue to a considerable extent without having any appreciable effect on the formation of BaP. However, additions of nitropropane brought about a 90 percent reduction in PAH production in the propane diffusion flames (and up to 75 percent reduction when burning No. 2 oil in a single-cylinder diesel engine). However, 5 volume percent of the nitropropane had to be added to achieve this amount of reduction. The same amount of nitroethane additive resulted in 64 percent reduction in PAH levels. The most effective agent that these investigators found was tertiary-butyl hydroperoxide which provided 92 percent reduction in PAH emission with the propane flame (and 90 percent reduction when used in a concentration of 2 volume percent in the diesel fuel).

A substantial reduction in the formation of BaP also was noted by Long and Ray⁽⁷²⁾ when they added nitroethane to commercial propane which was burned as a laminar diffusion flame in air. The air supply was reduced to give heavy soot formation in the absence of the additives, and under these circumstances it was found that as little as 0.05 moles of nitroethane per mole of fuel brought about an 83 percent reduction in the BaP formation. Doubling the concentration of the nitroethane increased the percent reduction only to 88 percent. These authors found that nitroethane reduced the BaP formation to a greater extent in the smoky propane flames than it did in the No. 2 oil mentioned previously.

The effect of methanol additions on ethylene diffusion flames was investigated by Chakraborty and Long⁽⁷³⁾ on the basis that only very small amounts of unsaturated compounds had been found in a methanol

diffusion flame. It was found that a modest reduction in soot, carbonaceous residue, chloroform soluble material, and total polycyclic aromatic hydrocarbons resulted. However, the PAH reduction amounted to only 18 percent when the menthanol concentration was 0.25 moles per mole of ethylene.

Significant reduction in polycyclic aromatic hydrocarbon formation also was observed by Spengler and Haupt⁽⁵⁷⁾ who studied the effects of additives on the combustion of mixtures of pentane and acetylene. The most effective additive was methyl-cyclopentadienyl manganese tricarbonyl, which reduced the BaP production by 97 percent when added at a rate of 2.5 grams of metal per liter of combustible vapor. While BaP production was greatly inhibited under these conditions, it must be noted that a relatively high concentration of the additive was used. When the additive concentration was reduced to 1.5 grams of metal per liter of combustible, the reduction in BaP was only 81 percent. Iron carbonyl was found to be less effective as an additive under their experimental conditions, providing only 50 percent reduction in BaP formation when added in a concentration of 2.5 grams of metal per liter of combustible vapor.

Investigations in I.C. Engines

A two-stroke gasoline engine was utilized by Kuhn and Tomingas⁽⁶⁴⁾ to study the effect of oxidation catalysts on the formation of BaP. The BaP in the engine exhaust was reduced by 66 percent by the addition of 1 weight percent of the manganese salt of versatic acid, which is a multibranched synthetic fatty acid containing C₉ to C₁₁ carbon chains. In other experiments, it was found that no BaP was produced when diisopropyl ether was used as a fuel.

Other studies have been reported in which the active agent either was not completely designated or was difficult to identify. Thus, for example, Hunigen and his colleagues⁽⁷⁴⁾ reported on the content of BaP in the exhaust gases of two-stroke engines. They found that the lubricating oil in the gasoline-oil mixture which was burned exercised an important influence on the BaP production. When the lubricating oil content of the mixture was 3 percent by volume, the BaP content of the exhaust gases was 40 percent less than without the lubricating oil. When the lubricating oil concentration was increased to 5 volume percent, the BaP formation was completely eliminated under the combustion conditions that were studied. The nature of the oil was not specified, and it is possible that some metal-containing compound in the oil was the active ingredient.

Negative results were obtained by Golothan⁽⁶⁵⁾ when an oil-soluble barium compound was added to diesel-engine fuel. There was no reduction in the level of PAH in the exhaust gases when the additive was used at a concentration of 0.1 weight percent.

In a general discussion of fuel additives, Van Den Heuvel⁽⁷⁵⁾ claimed that the addition of metal-containing combustion catalysts to a fuel would reduce the soot quantity produced, and also would reduce the concentration of PAH. In this connection, alkali metal compounds were mentioned as being most effective because the metal ions produced prevent the agglomeration of large soot particles from smaller particles of unburnt carbon. However, the author did not cite any quantitative data to support this contention.

Survey Conclusions Related to Use of
Combustion Additives for Reducing
Emissions of POM

Although only light oils and gases were involved in these research programs on POM, significant reduction in the POM production was reported in a number of cases. However, these data from gas flames and internal combustion engines may not be applicable to boiler emissions. Heavier fuels may respond differently to the few organic and organometallic compounds which were found effective. Further investigation of suitable additives appears to be warranted, using residual oil as fuel. (these investigations should use advanced POM measurement techniques and take into consideration the conditions encountered in typical combustion equipment.) The nitrogen-containing compounds previously found effective for POM are of questionable suitability for additive use, as they would add to NO_x emissions, but the transition metal compounds may be useful.

ADDITIVE EFFECTS ON SULFUR OXIDES

Much of the experimental work on additives for reduction of sulfur oxides in oil- and coal-burning systems has been directed at eliminating the corrosion and deposits which occur throughout the combustion system as a result of sulfur oxides. Although occasionally the effects of the additives on sulfur dioxide was noted in the literature, most of the effort was devoted to measurements of changes in sulfur trioxide concentration, particularly in terms of the sulfuric acid dew point. However, for the purposes of this review, such data have been converted to ppm SO_3 in the gases, using the data of Lisle and Sensenbaugh⁽⁷⁶⁾. Typically, the SO_2/SO_3 ratio is 30 to 100 depending on combustion conditions, especially excess air.

Because corrosion reduction in various parts of the boiler was usually the objective of the additive program, the compounds were introduced where it was thought that they would be most effective, often downstream of the combustion zone. For this reason, additives to reduce sulfur oxide concentrations sometimes were introduced in the superheater, in the convection passes, at the economizer, or at the air heater*. Investigations in which the additives were introduced downstream in this fashion, and the many studies of sulfur oxide removal by scrubbing systems are not covered in this review. In the investigation reviewed here, the additive was either introduced in the fuel or into the combustion zone. Pertinent research has been reported for both oil and coal firing, from laboratory burner scale to full-scale boiler trials.

* Additives that are active downstream of the flame zone are categorized as Type III Additives.

COMBUSTION ADDITIVES IN FUEL-OIL FIRING

EPA Investigation of Residual Oil Firing

An extensive experimental program to determine the effects of additives on sulfur oxide emissions from residual oil firing was carried out by Pershing, Martin, Berkau and Hall⁽²⁾ as part of an in-house investigation by the Environmental Protection Agency. Although the additives investigated were proprietary mixtures, a complete chemical and X-ray diffraction analysis identified the compounds involved.

The test system consisted of an instrumented commercial package boiler (1.8 million Btu/hr capacity) fired with an air-atomizing-type gun burner that was capable of modulation. The fuel contained 0.88-0.90 weight percent sulfur, and produced about 615 ppm of sulfur oxides in the flue gases. The additives were injected in powder form into the highly turbulent region of the combustion air stream just before the nozzle. In the course of the program, variations were made in excess air, boiler load, and additive dose rate. No reduction in total sulfur oxides occurred with any of the four additive systems investigated.

These were:

1. Clay mixture, consisting essentially of sodium or calcium aluminum silicates.
2. A mixture consisting chiefly of NaCl and CaO, with some MgO and Fe_2O_3 .
3. A mixture containing mostly NaCl, with some CaCO_3 , talc, and iron manganese silicate.
4. A clay mixture consisting of sodium and calcium aluminum silicates.

A comparison test with Na_2CO_3 at a feed rate of 1 pound per 30 pounds of fuel resulted in a 36 percent reduction in sulfur oxides by converting them to sodium sulfite and sulfate. This test demonstrated that

sulfur oxide reduction was possible in the combustion system used, and the negative results obtained with the other additives were valid. In the course of the experiments, it also was observed that the additives had no effect on emissions of NO, CO, hydrocarbons under any of the conditions investigated.

Other Investigations with Residual Oil Firing in Experimental Apparatus

Most of the other investigations of sulfur oxide removal by combustion zone additives have been concerned with the reduction of the SO_3 content of the gas stream, and the effects on SO_2 were not determined.

A significant program of this type was conducted by Rendle and Wilsdon⁽⁷⁷⁾, who used an experimental furnace which burned 6 to 10 pounds per hour of residual fuel oil. These investigators examined materials which could act to reduce sulfur oxides in any of three ways: (1) physical adsorption, (2) combination with atomic oxygen, or (3) neutralization of acidic gases. Representatives of each of these classes of materials were fed into the oil-fired experimental furnace with a combustion-chamber temperature of 1830 F and 25 percent excess air. The results of their experiments can be summarized as follows:

1. Materials which physically absorb gases. Powdered SiO_2 gave maximum of 50 percent reduction in SO_3 concentration, and carbon blacks did not change SO_3 concentration significantly when added to the fuel oil at concentrations up to 0.5 percent by weight.
2. Materials which combine with atomic oxygen. Tars containing pyridine and other organic nitrogen compounds did not change the SO_3 levels appreciably when used in amounts up to 2.7 percent.

3. Materials which neutralize acidic gases. Oil soluble magnesium and zinc naphthenates completely eliminated SO_3 from the gas stream. The magnesium compound was slightly more effective than the zinc derivative because only 0.15 weight percent of the magnesium compound was needed to eliminate SO_3 whereas 0.2 weight percent of the zinc compound was required. With magnesium oxide, 0.35 weight percent of the additive was needed to remove all the SO_3 . In the case of zinc dust, 0.45 weight percent was required, and for dolomite, 0.8 weight percent was needed. In each case the amount of additive required was equal to or greater than the stoichiometric amount required to react with the SO_3 in the gas stream. For compounds of the same metal, the oil-soluble materials proved to be more efficient.

In this study no measurement was made of the effects on SO_2 . However, some reduction in SO_2 concentration is inevitable when basic materials such as dolomite or MgO are used.

These results have been confirmed by other investigators in the laboratory and by actual practice in full-scale boilers. Flint and co-workers⁽⁷⁸⁾ using a small refractory furnace fired with residual oil, also showed that zinc naphthenates could be used to eliminate SO_3 from the gas stream. In their furnace system 0.07 weight percent of the zinc naphthenate reduced the SO_3 by 75 percent, while twice this amount of the zinc compound completely eliminated the SO_3 .

Peck and Zaczek⁽⁷⁹⁾ observed that metal oxides such as those of zinc, copper, magnesium, calcium, and aluminum all were capable of reducing the corrosive effects of sulfur oxides, but they did not make any quantitative measurements of the gas concentrations.

With a laboratory-scale burner using residual oil, Lewis⁽⁸⁰⁾ observed that SO_3 could be completely eliminated in his rig by the addition of 0.07 weight percent magnesium in the form of magnesium

naphthenate. He also tried an oil-soluble zinc compound, but found it to be less effective than the magnesium naphthenate.*

The mixture of hydrated MgO and Al_2O_3 having an Mg to Al ratio of 9 to 1, developed by G. K. Lee and his associates, mentioned previously, also has been effective for SO_3 reduction^(51, 81, 82). Results of additive trials in both laboratory combustion boilers and operating boilers demonstrated that SO_3 can be completely eliminated by use of the additive in a concentration of 0.1 volume percent in the oil.

Full-Scale Investigations with Residual Oil Firing in Utility Boilers

In full-scale boiler applications of additives, the Florida Power Corporation found dolomite to be effective. As reported by Huge and Plotter⁽⁸³⁾ at the Inglis Station, the addition of 1/10 weight percent of dolomite as a slurry in the fuel oil resulted in about 33 percent reduction in the SO_3 concentration. At the Higgins Station, the dolomite was introduced in the combustion air as a dry powder. In this case, 1/10 weight percent of dolomite reduced the SO_3 by 42 percent. However, doubling the amount of dolomite used gave only a 50 percent reduction in SO_3 .

The effects of additives in the boilers at the Marchwood Station in England were reported by Wilkinson and Clarke⁽⁸⁴⁾. In this case, residual oils containing up to 4.5 percent sulfur constituted the fuel. The addition of dolomite, which was introduced in the vicinity of the burners at a rate of 3 to 4 pounds per ton of fuel, brought about an 80 percent reduction in the SO_3 levels. Magnesium carbonate also was tried, and a 75 percent reduction in SO_3 was achieved with the addition

* Other studies with No. 2 oil by Altwicher and associates⁽⁸⁵⁾ demonstrated that cobalt and manganese naphthenate provided only small reduction (7 to 10 percent) in SO_3 concentration. Iron naphthenate gave no reduction.

of 1 to 2 pounds of additives per ton of fuel burned. An effort was made to use magnesium oxide similarly as an additive, but the fouling and clogging problems which resulted made its use ineffectual. Dolomite also has been found effective in Swedish boiler practice.

A favorable experience with magnesium oxide has been reported by Exley et al of the Long Island Lighting Company, where four separate power stations are combining the additive treatment with low-excess-air operation⁽⁸⁶⁾. In addition to reducing sulfuric-acid stack emissions, boiler efficiency was raised and reliability was improved. Magnesium vanadate was recovered from the deposits in the furnace; at the time of the report (1966), at least 1.5 times the cost of the additives was recovered through the sale of the vanadium by-product.

Granular magnesium metal (20 to 50 mesh) injected into the combustion zone was found by Reese et al⁽⁸⁷⁾ to be effective in reducing SO_3 in an oil-fired boiler. The unit in which the tests were made was rated at 185 megawatts and the magnesium was added at the rate of 12 pounds per hour. A 60 to 75 percent reduction in SO_3 was found, depending on what part of the system the measurements were made.

Lasch⁽⁸⁸⁾ reported success with injections of granular magnesium into the combustion chamber of oil-fired boilers at the Belvedere and Tidbury Power Stations of the Central Electricity Generating Board in England. With oil having a 2 to 4 percent sulfur content, magnesium injection at a rate of 0.4 pounds per ton of oil eliminated any problems with SO_3 .

Several stations of the Consolidated Edison Company that burn residual fuel oil have used methylcyclopentadienyl manganese tricarbonyl as an additive. The SO_3 in the flue gases was reduced by 45 percent, but the concentration in which the additive was used was not specified⁽⁸⁹⁾.

Additive trials conducted by the New England Power Company⁽⁵²⁾ showed that ferrocene, iron carbonyl, and manganese dioxide all were ineffective in reducing the SO_3 content in the flue gases. [Martin, Pershing, and Berkau⁽¹⁾, firing No. 2 oil in the EPA laboratory-scale burner, obtained similar negative results with ferrocene and with methylcyclopentadienyl manganese tricarbonyl.]

COMBUSTION ADDITIVES IN COAL FIRING

Only a relatively small amount of effort has been devoted to fuel additives or combustion-zone additives to reduce sulfur oxides in coal-fired systems.

In contrast, considerable investigation has been directed to downstream addition of limestone for sulfur oxide removal. The limestone must be added in a temperature zone in which it will calcine to CaO , which then reacts with sulfur oxides to form CaSO_3 and CaSO_4 . These systems have encountered serious problems with scaling and fouling. For example difficulties have been experienced in large-scale operation of limestone scrubbing at the Meramec Station of the Union Electric Company⁽⁹⁰⁾ and the Lawrence Station of Kansas City Power and Light⁽⁹¹⁾.

The following discussion is confined to investigation where the additive is introduced with the fuel or into the combustion zone.

Michel and Wilcoxson⁽⁹²⁾ observed that dolomite used at a rate of 7.5 pounds per ton of coal fired, reduced SO_3 concentration by 50 percent. Doubling the dolomite addition reduced the amount of SO_3 by 90 percent.

In a pulverized-coal burner, Borio, et al⁽⁹³⁾ observed a 65 percent reduction in the SO_2 concentration when NaOH was added to coal. The SO_3 level remained about the same. However, anomalous results were obtained when dolomite and NaOH were used in combination,

as the SO_2 concentration increased from 1200 to 2400 ppm. A similar effect was noted when CaO was added to the coal.

Corbett and Flint⁽⁹⁴⁾ added zinc ore concentrate to coal used in stoker-fired boilers at the Brimsdown Power Station. The zinc oxide smoke generated in this fashion eliminated the SO_3 from the flue gases when the additive was used at a concentration of 0.25 weight percent.

Powdered sodium carbonate was aspirated into the combustion zone of a large spreader-stoker coal-fired boiler in research by Brancaccio and Flach⁽⁹⁵⁾. The sulfur dioxide emissions were reduced up to 70 percent in this fashion. Sodium bicarbonate also was promising, but both of these additives created problems with boiler fouling.

A test unit consisting of a 750-horsepower boiler fired by a multiple retort underfeed stoker was used by Land and his colleagues⁽⁹⁶⁾. Additives were either mixed with the coal before it was fired or were injected with compressed air jets over the fire. Dolomite chips, pulverized dolomite, hydrated lime, aragonite, and red mud were used as additives. Anomalous results were obtained in the limited tests that were made, but the results did indicate that sulfur dioxide emissions from coal burning can be reduced somewhat by the use of additives introduced in this fashion.

A coal related study by Whittingham⁽⁹⁷⁾, using a coal gas burner with 1,000 ppm SO_2 added, showed that silicon-monoxide fume formed by the reduction of silicates with carbon could be used to reduce SO_3 concentration. At an additive concentration of 2 grains per cubic foot, the SO_3 was reduced by 80 percent. He also studied zinc-oxide fume⁽⁹⁸⁾. At a concentration of 2×10^{-6} grams of ZnO per liter, this additive gave an 85 percent reduction in the SO_3 level. In another study, Whittingham used coal-gas introduction above the flame to make a carbon smoke⁽⁹⁹⁾. The SO_3 content of the gas stream was reduced by 90 percent when a smoke concentration of 0.24 grains per

cubic foot was used. Whittingham suggested that the role of the smoke particules in reducing sulfur oxide concentration consisted of absorbing the gases by virtue of the large effective surface area of the fume. No measurement of particulates was made, however, to determine whether the introduction of fume would cause a significant increase in the emissions of particulate.

Survey Conclusions Related to the Use
of Combustion Additives for Reducing
Emission of Sulfur Oxides

Combustion additives containing basic element such as magnesium, calcium, and zinc are effective in reducing SO_3 by converting it into metal sulfates which can be removed as particulates or, possibly in some cases, by inhibiting the catalytic oxidation of SO_2 by exposed metal surfaces in the low-temperature regions of the boiler. These additives are particularly effective as oil-soluble compounds which can be mixed into fuel oils. However, these additives are not useful in reducing SO_2 in flue gases. Solids containing calcium and magnesium may be capable of reducing SO_3 from coal combustion. The use of additives may thereby reduce the potential for sulfuric-acid aerosol formation, although the total sulfur emitted may be unchanged.

ADDITIVE EFFECTS ON NITROGEN OXIDES

Most of the effort aimed at reduction of NO_x emissions has involved combustion control techniques. These methods require modification of the operating and design features which affect the various combustion parameters. However, some research has been conducted on the use of additives to reduce NO_x emissions. Some of this effort was directed primarily at NO_x , but in other cases the data on nitrogen oxide emissions were recorded in the course of a program whose main

objective was reduction of particulate emissions or sulfur oxides. All of these programs were carried out on liquid fuels; no data have been found for coal-fired systems where additive effects on NO_x have been recorded.

Investigations Firing Residual Oil in Boilers

Research on additives to residual oil used in low-pressure heating boilers was conducted by Lee, Friedrich, and Mitchell^(51, 81). They found that a mixture of partially dehydrated hydroxides of magnesium and aluminum having a 9 to 1 magnesium-aluminum ratio effected a 43 percent reduction in NO_x when added to the oil at a concentration of 0.1 volume percent. However, it was noted that the NO_x concentration, while decreasing with greater additive dosage, was at a higher level than with untreated oil until the dosage rate reached the 1/10 percent level.

Molino and Zobolotny⁽⁵²⁾ reported results by the New England Power Company where additions of ferrocene to residual oil fuel had no effect on the amount of NO_x produced. Iron carbonyl and manganese dioxide also were found to be without effect on nitrogen oxides.

Investigations Firing Distillate Oil in Laboratory Furnaces

In the very extensive EPA investigation of the effects of fuel additives on emissions from distillate-oil-fired furnaces, Martin, Pershing, and Berkau⁽¹⁾ found that the few additives which reduce particulate emissions had no effect on the NO_x emissions. This work was primarily concerned with proprietary additives, but two of the additives could be specifically identified as the chemical compounds biscyclopentadienyl iron (ferrocene) and methylcyclopentadienyl manganese tricarbonyl. Although they had no effect on NO_x , these two compounds were shown to have some efficacy in reducing particulate emissions.

One of the few studies directed mainly to nitrogen oxides was carried out by Altwicker, et al⁽⁸⁹⁾ who used No. 2 oil in a small laboratory burner. Additions of 0.5 and 1.0 volume percent of cobalt, manganese, and iron naphthenates reduced NO_x emissions only 6 to 15 percent. The cobalt compound was the most effective and the iron derivative the least effective. These investigators found the same small reduction in nitrogen oxides when using proprietary additives containing manganese. As might be expected, some commercial amine additives increased the production of nitrogen oxide.

Similar studies carried out by Fredette⁽¹⁰⁰⁾ showed that butanol and pentanol also would provide 10 to 15 percent reductions in nitrogen oxides when added to No. 2 oil at a concentration of 1 volume percent.

Investigation Directed to Gas Turbines

A broad experimental program for the U.S. Air Force reported by Shaw⁽¹⁰¹⁾, to assess the feasibility of reducing NO_x emissions from aircraft gas turbine engines, included a study of additive treatments. Jet fuel A was burned in a laboratory combustor. The selection of additives was systematized to cover the various mechanisms which could be hypothesized for reduction of NO_x formation. These mechanisms included:

1. Heterogeneous catalysts for either reduction or decomposition of NO_x
2. Oxygen atom scavengers
3. Temperature reducers via heat transfer with solids or endothermic physical conversion
4. Ignition delay agents
5. Agents that change spray dynamics
6. Agents that react with NO .

Over 70 additives were evaluated in this program. These included metal naphthenates and acetylacetonates, metal salts of neoacids, alkali, and

alkaline-earth metal carbonate suspensions, emulsions of alkali hydroxides, miscellaneous metal compounds, and various organic compounds. The additives falling in the first category, namely, heterogeneous catalysts, proved to be most effective in reducing NO_x emissions. However, the greatest reduction obtained was only 30 percent, which was achieved by adding cobalt or manganese naphthenate at a concentration of 0.5 weight percent metal. The iron and copper naphthenates were somewhat less effective. The only other effective compound was the zirconium salt of neodecanoic acid which reduced nitrogen oxides by 22 percent at a concentration of 0.2 weight percent. Other organometallic compounds containing calcium, cerium, lead, aluminum, lithium, or antimony did not reduce NO_x significantly. Four suspensions of metal carbonate in a diluent oil were added in amounts of 0.1 percent by weight metal; sodium carbonate reduced nitrogen oxides by about 16 percent and lithium carbonate, by about 10 percent. The other carbonates, barium and calcium, were not effective.

Of the 16 homogeneous additives, which were all organic compounds, only n-butylmercaptan was effective in Shaw's investigation. This compound reduced NO_x by about 11 percent. Any organic compounds containing nitrogen were found to increase the emissions. Various inorganic salts which were dissolved in water and then emulsified in the jet fuel, had no effect, but those of alkali hydroxides gave small reductions. The best of these was 0.1 weight percent sodium as sodium hydroxide, which gave 16 percent reduction in nitrogen oxides. The only other water emulsion that showed some promise in reducing NO_x was one that contained 37 ppm by weight hydrazine acetate. The results with this emulsion were erratic, but in some replicate experiments, gave as much as 16 percent NO_x reduction.

It was concluded that no really effective additive had been uncovered in this work.

Investigation Directed to Diesel Engines

In a diesel engine study, McCreath⁽¹⁰²⁾ found that isoamyl nitrate addition to the fuel provided about a 17 percent reduction in NO_x , while ditertiary-butyl peroxide gave a 14 percent reduction. He also noted that if the additive were mixed with the fuel and left to age, some reaction occurred which improved slightly the performance of the additive. Under these conditions, nitromethane reduced nitrogen oxides about 9 percent, whereas in a fresh mixture, it actually increased the production of NO_x . The nature of the chemical changes involved was not investigated.

Survey Conclusions Related to Use of Combustion Additives for Reducing NO_x

Small reductions in NO_x emissions have been observed with a variety of additive types. Oil-soluble transition-metal compounds, organic compounds, and magnesium oxide all provide minor reduction effects. However, it appears that there is little evidence of achieving any worthwhile benefits for NO_x control by the use of fuel additives.

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The reader is referred to the SUMMARY at the beginning of this report, especially the Section on "Overview and Conclusions" which combine observations from the analysis of basic combustion mechanisms in Part I with the review of experimental investigations in Part II. Also included there are comments on the overall perspective of possible limitations to the use of additives.

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